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Optical Properties of Reactive RF Magnetron Sputtered Polycrystalline Cu_3N Thin Films Determined by UV/Visible/NIR Spectroscopic Ellipsometry: An Eco-Friendly Solar Light Absorber

E. Márquez ^{1,*}, E. Blanco ¹, M. García-Gurrea ¹, M. Cintado Puerta ¹, M. Domínguez de la Vega ¹, M. Ballester ², J. M. Manuel ¹, M. I. Rodríguez-Tapiador ³ and S. M. Fernández ³

¹ Department of Condensed-Matter Physics, Faculty of Science, University of Cadiz, 11510 Puerto Real, Spain; eduardo.blanco@uca.es (E.B.); marcos.garciagu@alum.uca.es (M.-G.G.); manuel.cintadopuerta@alum.uca.es (M.C.P.); manolo.dominguez@uca.es (M.D.d.I.V.); jose.manuel@uca.es (J.M.M.)

² Department of Computer Sciences, Northwestern University, 633 Clark St., Evanston, IL 60208, USA; manuelballestermatito2021@u.northwestern.edu

³ Environmental and Energetic Devices Unit, Energy Department, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Avenida Complutense 40, 28040 Madrid, Spain; mariaisabel.rodriguez@ciemat.es (M.I.R.-T.); susanamaría.fernandez@ciemat.es (S.M.F.)

* Correspondence: emilio.marquez@uca.es



Citation: Márquez, E.; Blanco, E.; García-Gurrea, M.; Cintado Puerta, M.; Domínguez de la Vega, M.; Ballester, M.; Manuel, J.M.; Rodríguez-Tapiador, M.I.; Fernández, S.M. Optical Properties of Reactive RF Magnetron Sputtered Polycrystalline Cu_3N Thin Films Determined by UV/Visible/NIR Spectroscopic Ellipsometry: An Eco-Friendly Solar Light Absorber. *Coatings* **2023**, *13*, 1148. <https://doi.org/10.3390/coatings13071148>

Academic Editor: Octavian Bui

Received: 17 May 2023

Revised: 12 June 2023

Accepted: 15 June 2023

Published: 25 June 2023



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Abstract: Copper nitride (Cu_3N), a *metastable* poly-crystalline semiconductor material with reasonably high stability at room temperature, is receiving much attention as a very promising next-generation, earth-abundant, thin film solar light absorber. Its *non-toxicity*, on the other hand, makes it a very attractive *eco-friendly* (greener from an environmental standpoint) semiconducting material. In the present investigation, Cu_3N thin films were successfully grown by employing reactive radio-frequency magnetron sputtering at room temperature with an RF-power of 50 W, total working gas pressure of 0.5 Pa, and partial nitrogen pressures of 0.8 and 1.0, respectively, onto glass substrates. We investigated how argon affected the optical properties of the thin films of Cu_3N , with the aim of achieving a low-cost solar light absorber material with the essential characteristics that are needed to replace the more common silicon that is currently in present solar cells. Variable angle spectroscopic ellipsometry measurements were taken at three different angles, 50°, 60°, and 70°, to determine the two ellipsometric parameters ψ , Δ . The bulk planar Cu_3N layer was characterized by a one-dimensional graded index model together with the combination of a Tauc–Lorentz oscillator, while a Bruggeman effective medium approximation model with a 50% air void was adopted in order to account for the existing surface roughness layer. In addition, the optical properties, such as the energy band gap, refractive index, extinction coefficient, and absorption coefficient, were all accurately found to highlight the true potential of this particular material as a solar light absorber within a photovoltaic device. The *direct* and *indirect* band gap energies were precisely computed, and it was found that they fell within the useful energy ranges of 2.14–2.25 eV and 1.45–1.71 eV, respectively. The atomic structure, morphology, and chemical composition of the Cu_3N thin films were analyzed using X-ray diffraction, atomic force microscopy, and energy-dispersive X-ray spectroscopy, respectively. The Cu_3N thin layer thickness, profile texture, and surface topography of the Cu_3N material were characterized using scanning electron microscopy.

Keywords: copper nitride semiconductor; RF magnetron sputtering; spectroscopic ellipsometry

1. Introduction

Transition metal nitride thin film materials such as copper nitride (Cu_3N) exhibit very attractive and remarkable physical properties, such as electrical, optical, and energy-storage

properties, which allow this particular material to be employed in many technological application fields [1,2]. Consequently, copper nitride has drawn a great deal of attention as a new *eco-friendly* (greener from an environmental standpoint) solar absorber material for use in flexible and lightweight thin film photovoltaic cells [3,4]. This earth-abundant, non-toxic, metastable semiconducting material's band gap can potentially be easily adjusted depending on the manufacturing conditions and growth techniques and both the manufacturing conditions and deposition techniques. Among the fields of applications, the material can be included in the following: integrated circuits, photo-detectors, optoelectronics, and energy-conversion applications [5–7]. Emphasizing again the above-mentioned specific use of Cu_3N as a novel *solar* absorber thin-layer material for photovoltaic cell technology [8], its development has garnered notable interest, with the goal being to introduce it into novel designs within the next future generation of cost-effective solar cells. This recently-gained attention as a *light* absorber in solar cells is mainly based upon its above-mentioned clear non-toxicity and significant earth abundance, which result in it being an environmentally friendly material. Furthermore, the theoretically predicted band gap value for Cu_3N is approximately 0.9 eV [9,10], but its experimentally obtained values for indirect and direct band gaps have been found to be within energy values ranging from 1.17 eV to 1.69 eV and from 1.72 eV to 2.38 eV, respectively [10,11]. These calculated values imply that the copper nitride semiconductor must be considered as a promising candidate for next-generation light absorbers, that is, it must be considered as a viable option to totally replace the more common silicon that is currently used in the solar cell sector.

Such a large range in the reported differences of the band gap energy could be explained as a possible difference in the stoichiometry of the Cu-N binary system and also due to the existence of oxygen impurities inside the crystal lattice. This particular material, on the other hand, interestingly possesses an extremely high absorption coefficient that is larger than 10^5 cm^{-1} above approximately 2.0 eV [12], as will be accurately found in this work, which underlines once more its above-mentioned potential role as an solar light absorber for photovoltaic cell technologies.

In the present investigation, the complex index of refraction of the Cu_3N thin films was determined via variable angle spectroscopic ellipsometry (VASE) measurements [13], which were carried out at different angles of incidence to obtain the two ellipsometric parameters ψ (ψ) and Δ (Δ). In order to find a remarkable fit with the measured values of ψ and Δ , it is of paramount importance to propose a valid optical model. In our particular case, a one-dimensional *graded index* model was used throughout the whole layer from bottom to top, which was combined with a mixture of one Tauc–Lorentz (TL) oscillator [14–19] and up to four Gaussian (Gau) oscillators; these were successfully chosen to account for the *bulk* copper-nitride layer. A Bruggeman effective medium approximation (BEMA) model [20] was selected in order to describe the existing surface roughness layer. As a result, the optical constants of the Cu_3N thin layers were accurately obtained in the measured UV/visible/NIR spectral range. Our constructed optical model for determining the optical functions of Cu_3N thin layers is similar to the optical model suggested by Yan et al. [21–23] for the particular case of cesium lead bromide (CsPbBr_3) thin films, where the authors also adopted a similar combination of several TL and Gau oscillators and the front rough superficial layer was added to the model as well. More details will be provided later in the paper.

Finally, as a way of expressing the problem statement, it must be pointed out that there is generally very inconsistent and ambiguous information about the optical properties (especially regarding the refractive index) of copper nitride thin films, which is most likely caused by the existing differences in the particular synthesis technology that is employed in each particular case. All of the differences clearly represent an important disadvantage. Hence, it is particularly relevant and clarifying that the present spectro-ellipsometric study of the refractive index, n , extinction coefficient, k , and absorption coefficient α in the UV/visible/NIR spectral range were carried out in this work, which is

very scarce in the literature. This is the main novelty of the present work and the reason why it was undertaken.

2. Experimental Procedure: Materials and Methods

The growth of the Cu_3N thin films was performed by employing a commercial MVSystem LLC (Golden, CO, USA) single-chamber sputtering system, where the gun was radio frequency (RF) operated and was vertically movable. The transparent substrates that were employed were Corning glass 1737F (Corning Inc, USA). The 3-inch diameter and 6-millimeter thick target of Cu_3N was manufactured by Lesker Company (St. Leonards-on-Sea, UK), and it had a 99.99% purity. The glass substrate, on the other hand, was cleaned using an ultrasonic bath with ethanol and deionized water for 10 min, and it was lastly immersed in isopropyl alcohol; by blowing nitrogen on the substrates, all of the utilized glass substrates were thoroughly dried. The reactive RF sputtering process chamber was pumped down to a base pressure of 10^{-5} Pa, and the environment's total working gas pressure was set at 5.0 Pa during the deposition procedure; it was controlled by using a butterfly-type valve. The target-to-substrate distance was always adjusted to be conveniently selected at nearly 10 cm. The RF power was set to 50 W, and the corresponding growth time was 60 and 90 min. Every thin film growth took place at ambient temperature. The complete set of the growth conditions of our specimens are listed in Table 1.

Table 1. Deposition conditions for the growth of Cu_3N using RF magnetron sputtering deposition.

Growth Conditions						
Sample ID	Total Pressure (Pa)	N_2 Flux (sccm)	Ar Flux (sccm)	Partial N_2 Pressure	RF Power (W)	Deposition Time (min)
#1360	5.0	20	10	0.8	50	60
#1460	5.0	20	0	1.0	50	60
#1490	5.0	20	0	1.0	50	90

It should be highlighted that the atomic structure, morphology, and chemical composition of the Cu_3N thin films were analyzed using X-ray diffraction (XRD), atomic force microscopy (AFM), and energy-dispersive X-ray spectroscopy (EDX) techniques, respectively. The *polycrystalline* structure of the Cu_3N samples were studied by using the corresponding XRD diffraction patterns and measured using a PANalytical power diffractometer, X'Pert MPD/MRD model, and CuK_α radiation ($\lambda = 1.54 \text{ \AA}$). The scanned 2θ range was $10\text{--}60^\circ$, with a step size of 0.1° . The topography of the Cu_3N film surface was measured using a standard AFM microscope (Dimension Icon, Bruker, USA) in the peakForce tapping mode and Bruker SeanAsyst-Air probes (radius 5 nm). The surface roughness of the thin film samples was estimated by its root-mean-square value. Finally, the normal incidence optical transmission spectra were measured by employing a UV/visible/NIR, double-beam, Perkin-Elmer Lambda-1050 spectrophotometer and a single-beam VASE spectroscopic ellipsometer.

Lastly, the Cu_3N thin-layer thickness, profile texture, and surface topography of the Cu_3N material were characterized via scanning electron microscopy (SEM). As a first step, the samples were mechanically cleaved in order to obtain SEM micrographs from the cross-section profiles along the growth direction, which allowed for the determination of the average thickness of each Cu_3N layer. Afterwards, gold thin layers were deposited on all samples surfaces to avoid charging effects as a result of the electron beam's contact with the sample. This was achieved by using a magnetron deposition process via plasma in a 208HR-Cressington Sputter Coater (Cressington Scientific Instruments, Watford, UK). It should also be added that the relevant experimental detail of the thickness of the very thin gold layer that was coated during the SEM analysis was just a few nanometers.

The spectro-ellipsometric spectra ψ and Δ were measured over the spectral range of 300–2200 nm with steps of 10 nm at room temperature by making use of a Woollam

V-VASE spectroscopic ellipsometer. Together with a Berek computer-controlled, adjustable MgF_2 waveplate retarder, it functions effectively as a rotating, analyzing, variable-angle spectroscopic ellipsometer (the so-called *automatic retarder*). It is used over a broad spectral range to properly add a beam path delay. This variable retarder allows for the convenient adjustment of the input polarization in order to provide a reflected beam, which is always close to the circular polarization; thus, the system will measure Δ accurately over the whole angular range of $0\text{--}360^\circ$. Moreover, the *autoretarder* ellipsometer configuration allows for the measurement of the “%-depolarization”, which can be associated with thickness nonuniformities in the studied specimens. In these particular circumstances, this method allows for a better fitting of the two ellipsometric angles ψ and Δ . The Woollam WVASE program was used to analyze the experimental data rigorously [24].

3. Preliminary Structural and Morphological Characterizations

The XRD patterns of three as-deposited Cu_3N thin films are shown in Figure 1. The main diffraction peaks, identified as the (1 0 0), (1 1 1), and (2 0 0) crystallographic planes, represent a *polycrystalline* Cu_3N film (card number 00-047-1088) in *cubic*, *anti*- ReO_3 structures (space group $\text{Pm}\bar{3}\text{m}$, number 221, first reported by Juza and Hahn [25]). No evidence whatsoever for Cu phase and CuO formation was found in the present XRD diagrams. Moreover, the inset of Figure 1c displays the very prominent Raman peak at nearly 645 cm^{-1} , which is associated with the *stretching* of the Cu-N chemical bond [2].

As it was previously mentioned, the surface morphology of the Cu_3N thin film samples was carefully analyzed using AFM microscopy. Figure 2 displays the $1.0\text{ }\mu\text{m} \times 1.0\text{ }\mu\text{m}$ and $2.0\text{ }\mu\text{m} \times 2.0\text{ }\mu\text{m}$ bi-dimensional AFM micrographs of the three Cu_3N layers, with all of them being sputtered at a *total* gas pressure of 5.0 Pa. Table 2 indicates the values of the three considered surface roughness parameters S_q , S_a , and S_z , respectively, which were determined with the help of the software that was connected to this device and by using the 2D-AFM images displayed in Figure 2. It should be stressed that all of these calculations led to an estimated uncertainty of less than around 10%. According to the three measured surface roughness parameters S_q , S_a , and S_z , the *as-deposited* Cu_3N thin-layer samples under study certainly did exhibit a *relatively large* surface roughness.

Table 2. Surface roughness parameters determined from AFM $1.0\text{ }\mu\text{m} \times 1.0\text{ }\mu\text{m}$ and $2.0\text{ }\mu\text{m} \times 2.0\text{ }\mu\text{m}$ images of the copper nitride thin layer, which were grown by RF magnetron sputtering on glass substrates. Values of the root-mean-square height S_q , arithmetical mean height S_a , and maximum height S_z correspond to the two representative Cu_3N thin film samples.

Cu_3N Thin Film Sample ID	#1360	#1460	#1490
Figure ID	(a)	(b)	(c)
AFM Scanning Area	$1.0\text{ }\mu\text{m} \times 1.0\text{ }\mu\text{m}$	$1.0\text{ }\mu\text{m} \times 1.0\text{ }\mu\text{m}$	$2.0\text{ }\mu\text{m} \times 2.0\text{ }\mu\text{m}$
S_q (Root-Mean-Square Height), nm	16.5	6.6	18.0
S_a (Arithmetical Mean Height), nm	13.2	5.3	14.5
S_z (Maximum Height), nm	125	52.7	122
Cu_3N Thin Film Sample ID	#1360	#1460	#1490
Figure ID	(d)	(e)	(f)
AFM Scanning Area	$3.3\text{ }\mu\text{m} \times 3.3\text{ }\mu\text{m}$	$5.0\text{ }\mu\text{m} \times 5.0\text{ }\mu\text{m}$	$5.0\text{ }\mu\text{m} \times 5.0\text{ }\mu\text{m}$
S_q (Root-Mean-Square Height), nm	19.1	7.3	19.9
S_a (Arithmetical-Mean Height), nm	14.4	5.3	16.0
S_z (Maximum Height), nm	163.6	94.1	159.5

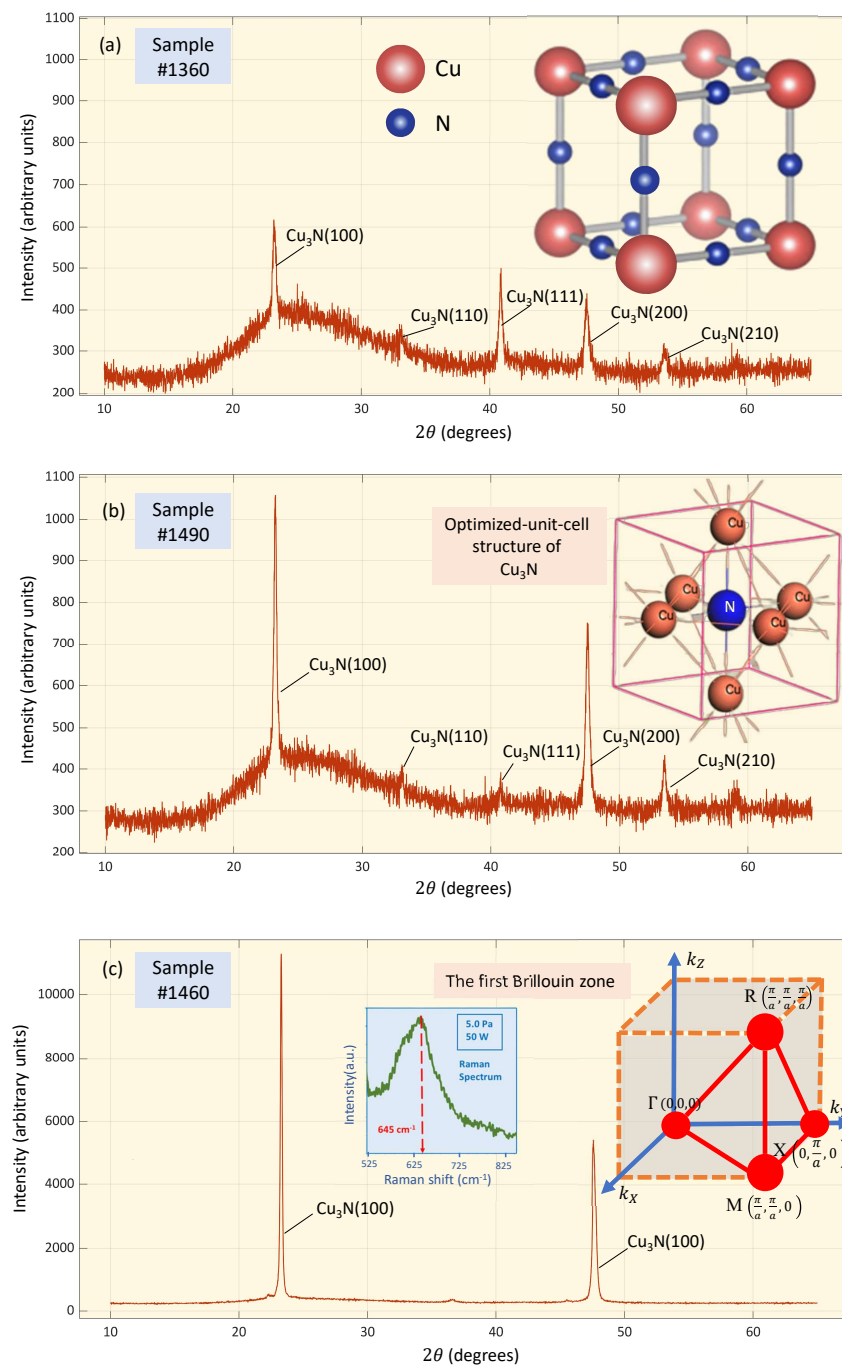


Figure 1. X-ray diffraction (XRD) patterns of the three copper nitride thin films, which were deposited onto glass substrates and specifically correspond to (a) specimen #1360, (b) specimen #1490, and (c) specimen #1460. The 3D cubic structure of Cu_3N is clearly illustrated as an inset in Figure 1b. This cubic structure of the *unit cell* contains six Cu atoms, and their fractional coordinates are the following: $(0, 0.5, 0.5)$, $(0.5, 0, 0.5)$, and $(0.5, 0.5, 0)$. The fractional coordinate of the N atom is $(0.5, 0.5, 0.5)$, which is in the center position of the present Cu molecules [26]. The *first Brillouin zone* of Cu_3N , with the high-symmetry points $\Gamma(0, 0, 0)$, $M(\frac{\pi}{a}, \frac{\pi}{a}, 0)$, $R(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$, and $X(0, \frac{\pi}{a}, 0)$, are labeled and joined by red lines [27] and is shown as an inset in Figure 1c. Moreover, in subfigure 1c, the corresponding Raman spectrum of a representative thin film sample of Cu_3N is presented, which was prepared at an RF power of 50 W and at a total gas pressure of 5.0 Pa.

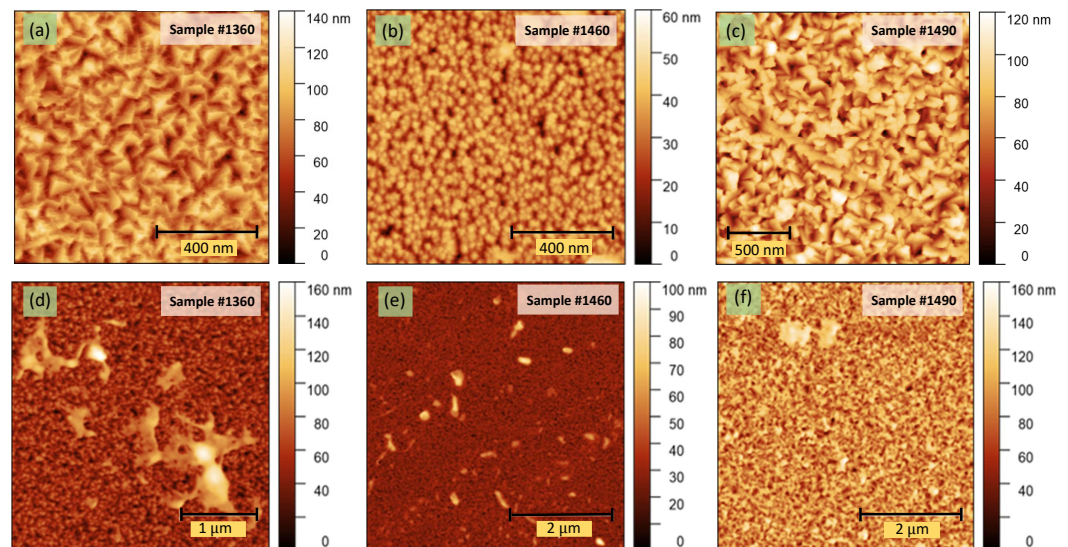


Figure 2. The two-dimensional AFM images of the Cu_3N thin films: (a,d) sample #1360, (b,e) sample #1460, (c,f) sample #1490, respectively.

It is reasonable, therefore, that the corresponding values obtained by the ellipsometric models for the BEMA surface roughness layer d_{rough} (see Table 3) are *larger* than those determined by the $1.0\ \mu\text{m} \times 1.0\ \mu\text{m}$ and $2.0\ \mu\text{m} \times 2.0\ \mu\text{m}$ AFM images. That is, taking into account the fact that the size of the light spot of the spectroscopic ellipsometer is very much larger than that of the previous AFM images, it is indeed likely to occur that d_{rough} would be larger than the three parameters S_q , S_a , and S_z , respectively.

Figure 3, on the other hand, shows cross-sectional-view SEM images of the as-grown Cu_3N thin layers; deposition occurred in a $\text{N}_2 + \text{Ar}$ environment (Figure 3a) in the particular case of the sample #1390 and without Ar in the case of sample #1490. The SEM-measured values of the film thickness clearly confirm the excellent accuracy of the layer thickness that was calculated by the UV/visible/NIR spectroscopic ellipsometry, as will be shown in detail below. The SEM images also corroborated that the film surfaces were not extremely rough and nonuniform and were mainly composed of typical *columnar* grains, which is typical of the present sputtering deposition technique [28]. Importantly, all of the results found by the SEM microscopy are certainly consistent with those found from the previous AFM microscopy analysis.

Furthermore, in order to register SEM images that reveal the Cu_3N layer texture, micrometric trenches were made transversely to the surface. This was carried out using a Ga^+ -ion beam via a focused ions beam (FIB) module. SEM images were recorded using secondary electron detectors, 5 kV accelerating voltages, and working distances ranging from 6 to 7 mm. Furthermore, the chemical composition of the Cu_3N films were found by using an electron dispersive X-ray spectroscopy module, which was attached to the electron microscope. EDX spectra were obtained by using electron probes accelerated at 30 kV voltages.

Table 3. Deposition conditions of the Cu₃N layers. The values of best fit parameters were obtained by employing the VASE ellipsometer (J.A.Woollam Co.) and their corresponding experimental uncertainties.

Sample #1360					
Cu ₃ N Visible and UV Oscillator Coefficients					
Oscillator	Type	A, amplitude	E ₀ , eV	C, eV	E _g , eV
1	Tauc–Lorentz	0.707 ± 0.4	1.12 ± 0.01	0.367 ± 0.03	0.751 ± 0.01
Oscillator	Type	A, amplitude	E ₀ , eV	Br, eV	
2	Gaussian	5.19 ± 0.1	3.94 ± 0.03	1.43 ± 0.1	
3	Gaussian	4.64 ± 0.02	2.62 ± 0.02	1.00 ± 0.05	
4	Gaussian	0.50 ± 0.09	1.80 ± 0.01	0.57 ± 0.09	
MSE: 4.007 d_{rough} : 41.6 ± 0.2 nm d_{bulk} : 388.4 ± 0.4 nm Thickness variation: 2.3 ± 0.3% Index variation: −13.2 ± 0.02% Offset, $\epsilon_{1\infty}$: 2.82 ± 0.05 E_u : 96 meV					
Sample #1490					
Cu ₃ N Visible and UV Oscillator Coefficients					
Oscillator	Type	A, amplitude	E ₀ , eV	C, eV	E _g , eV
1	Tauc–Lorentz	9.33 ± 0.4	2.46 ± 0.01	0.765 ± 0.03	0.872 ± 0.02
Oscillator	Type	A, amplitude	E ₀ , eV	Br, eV	
2	Gaussian	4.69 ± 0.1	3.96 ± 0.06	2.79 ± 0.06	
MSE: 6.686 d_{rough} : 46.1 ± 0.2 nm d_{bulk} : 563.7 ± 0.7 nm Thickness variation: 5.2 ± 0.1% Index variation: −14.1 ± 0.02% Offset, $\epsilon_{1\infty}$: 2.39 ± 0.06 E_u : 242 meV					
Sample #1460					
Cu ₃ N Visible and UV Oscillator Coefficients					
Oscillator	Type	A, amplitude	E ₀ , eV	C, eV	E _g , eV
1	Tauc–Lorentz	35.0 ± 4.3	2.50 ± 0.029	1.29 ± 1.16	1.56 ± 0.01
Oscillator	Type	A, amplitude	E ₀ , eV	Br, eV	
2	Gaussian	1.82 ± 1.0	4.25 ± 0.11	0.540 ± 0.41	
3	Gaussian	1.33 ± 0.91	4.19 ± 0.83	2.53 ± 0.60	
4	Gaussian	0.153 ± 0.07	1.94 ± 0.036	0.196 ± 0.08	
MSE: 9.738 d_{rough} : 22.1 ± 0.3 nm d_{bulk} : 310.4 ± 0.5 nm Thickness variation: ≈ 0 % Index variation: −4.81 ± 0.2% Offset, $\epsilon_{1\infty}$: 2.82 ± 0.05 E_u : 176 meV					

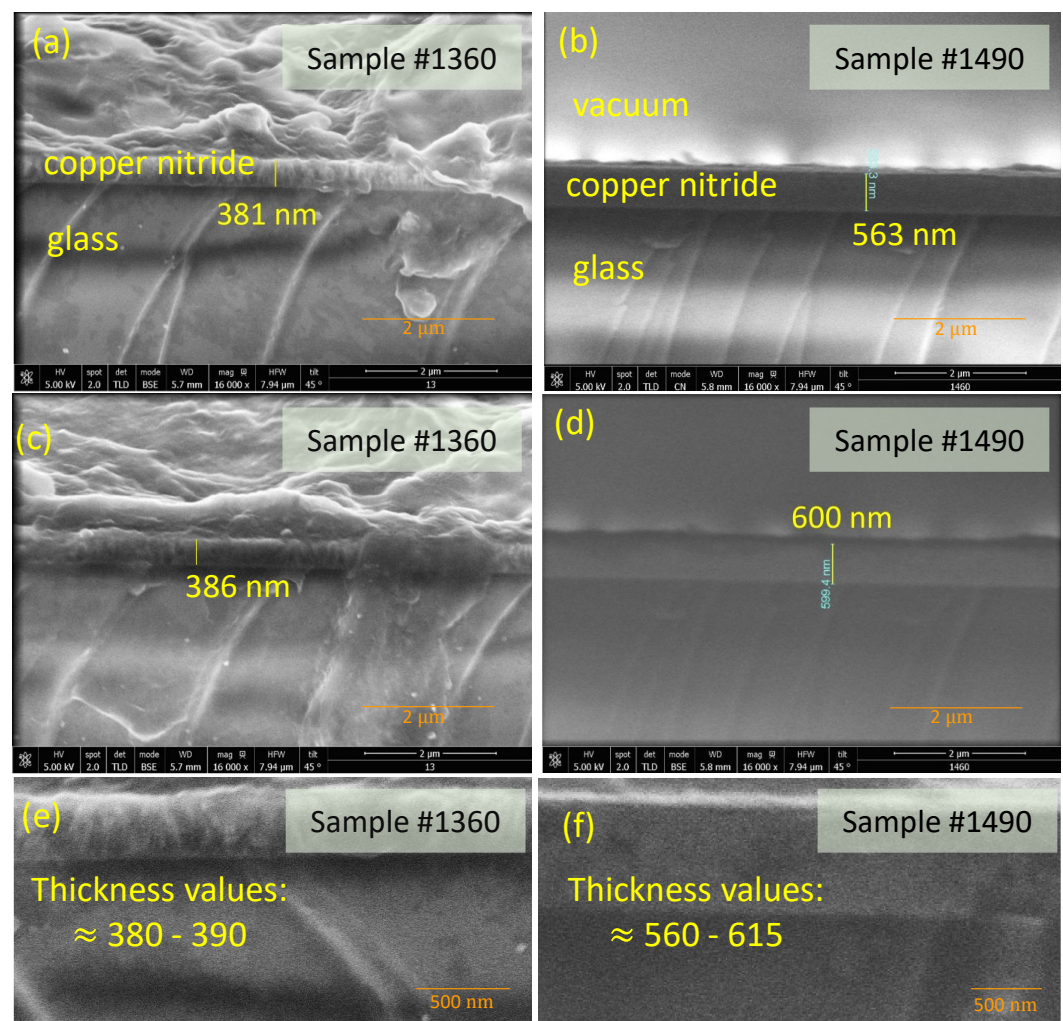


Figure 3. High-magnification cross-sectional SEM images of the studied in (a) N₂ + Ar, (specimen #1360), and (b) pure N₂ (specimen #1490) environments, (c) thickness of sample #1360 at different position, (d) thickness of sample #1360 with a higher magnification, (e) the same increased magnification for sample #1360, and (f) the same increased magnification for sample #1490. In these last two cross-sectional images the range of measured thickness are given.

We performed the conventional FIB sample-preparation procedures before undertaking the EDX analysis. In our EDX study of the present Cu₃N thin film specimens (see the measured EDX maps displayed in Figure 4), oxygen and nitrogen, as light elements, were *not* detected with high sensitivity; however, it can be observed that the oxygen signal was indeed more intense near the glass-substrate region (the glass having both silica and alumina). The nitrogen signal, on the other hand, notably decreased near the Cu₃N–glass interface and contrarily increased in the *bulk* Cu₃N layer. However, it must be pointed out that an increase in oxygen content and decrease in nitrogen content near the surface of the film was *not* observed. Significantly, from the present EDX maps (Figure 4), it is *not* reasonable to speculate the existence of a very thin copper oxide layer at the surface of the Cu₃N thin film.

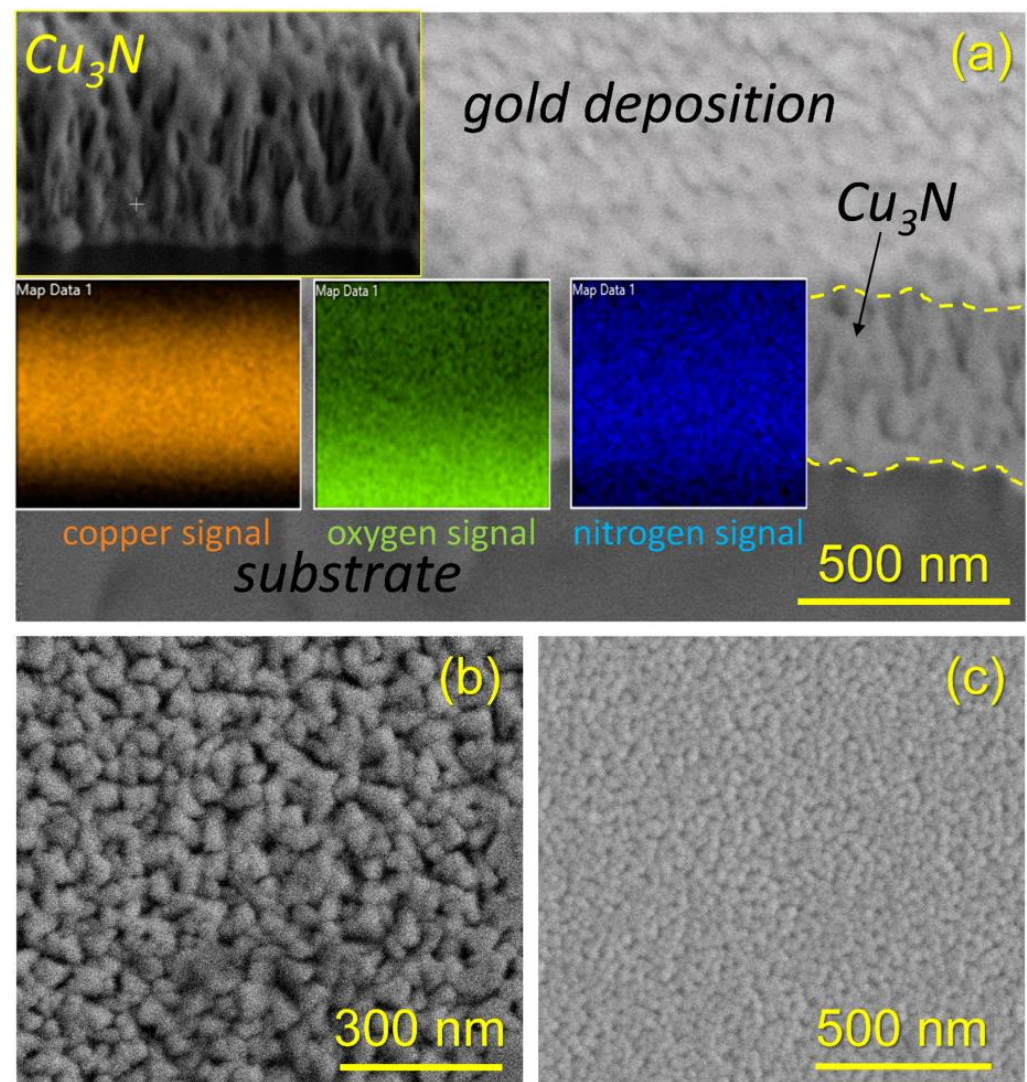


Figure 4. (a) Cross-sectional energy-dispersive X-ray (EDX) spectroscopy elemental mapping by performing a scanning electron microscopy (SEM) of copper nitride thin films, which were grown by RF magnetron sputtering on transparent glass substrates at room temperature. We have previously performed the FIB sample preparation before taking the EDX measurements. (b) SEM micrograph for a planar view of the surface of sample #1360 and (c) sample #1460.

Finally, Figure 4b,c shows the SEM topography of the surfaces of two representative as-deposited Cu_3N thin films. All of the images of the AFM and SEM microscopies have clearly demonstrated the *consistency* of the Cu_3N thin layers, which have a desired film surface morphology.

4. WVASE® Model Ellipsometric Fitting

In order to determine the optical constants n and k of the Cu_3N thin films, a commercial software package (WVASE version 3.942, J.A.Woollam), was used to construct a suitable model in order to fit the ellipsometric data ψ and Δ . It is certainly well-known that an *ideal* thin film must be homogeneous and must have a perfect flat surface, which very infrequently happens in reality. The most often found cases are obviously *non-ideal* thin films, with surface roughness at the top, thickness non-uniformity, and an optical constant variation from the top, down to the bottom, and through the whole thin film thickness [24].

The two ellipsometric angles ψ and Δ are related to the ratio of the Fresnel reflection coefficients R_p and R_s for p- and s-polarized light, respectively, as expressed in Equation (1):

$$\rho \equiv \frac{R_p}{R_s} = \tan(\psi)e^{i\Delta}. \quad (1)$$

The ratio ρ of the two values is measured using the VASE technique; as a consequence, the obtained values are very accurate and are reproducible [24]. For the present thin film sample under study (a Cu_3N thin film onto a thick transparent glass substrate), the Sellmeier dispersion function is employed in order to describe the optical properties of the transparent glass substrate. In the optical model for the Cu_3N thin film, such a film is divided into two equivalent parts.

One of them is a *bulk* planar Cu_3N layer, and its corresponding bulk thickness is denoted by d_{bulk} . The other one is a surface roughness layer, which consists of a mixture of voids and Cu_3N bulk layer material; the thickness of the vertical surface roughness is denoted by d_{rough} . To clearly illustrate the proposed model, a schematic sketch of this model is shown in Figure 5. For the surface roughness layer, a Bruggeman effective medium approximation is commonly appropriate, whereby the medium consists of the mixture of x % of voids and $(100 - x)$ % Cu_3N material and where it is verified that $0 < x < 100$. For the Cu_3N layer (with thickness d_{bulk}), the Tauc–Lorentz (TL) and Gaussian (Gau) oscillators were successfully adopted to accurately describe the complex dielectric function of the Cu_3N material [23,29]. The “TL” and “Gau” oscillator functions are provided by Equations (2)–(8), respectively [24]:

$$\epsilon_{n_T-L} = \epsilon_{n1} + i\epsilon_{n2}, \quad (2)$$

where:

$$\epsilon_{n2} = \begin{cases} \frac{A_n E_{on} C_n (E - E_{gn})^2}{(E^2 - E_{on}^2)^2 + C_n^2 E^2} \cdot \frac{1}{E}, & \text{if } E > E_{gn} \\ 0, & \text{if } E \leq E_{gn} \end{cases} \quad (3)$$

and

$$\epsilon_{n1} = \frac{2}{\pi} \mathcal{P} \int_{E_{gn}}^{\infty} \frac{\xi \epsilon_{n2}(\xi)}{\xi^2 - E^2} d\xi. \quad (4)$$

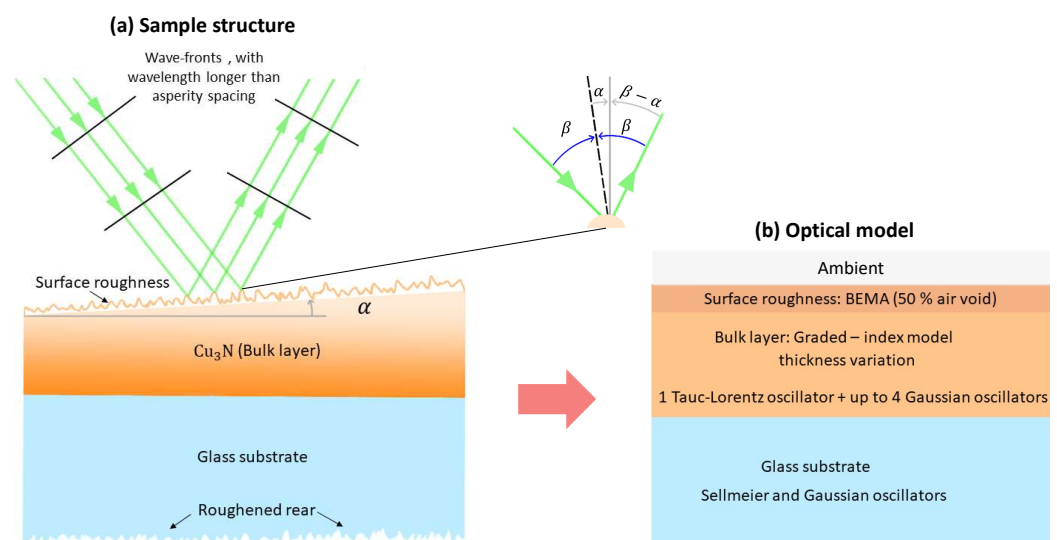


Figure 5. (a) Schematic diagram of the sample structure under study, consisting of a copper nitride thin film onto a transparent glass substrate, with the rear surface roughened. (b) Adopted model for the fitting carried out in the present ellipsometric analysis.

In Equations (2) and (3), the subscript “T-L” encompasses the fact that this particular dispersion model is based upon the Tauc joint density of states and Lorentz oscillator. The

four fitting parameters are A_n , E_{on} , C_n , and E_{gn} , respectively, and all of these parameters are expressed in eV. Here, $\mathcal{P}$ stands for the Cauchy principal value of the two previous integrals.

The “Gau” oscillator function, on the other hand, is provided by the following expression:

$$\epsilon_{n_Gau} = \epsilon_{n1} + i\epsilon_{n2}, \quad (5)$$

where:

$$\epsilon_{n2} = A_n e^{((E-E_n)/\sigma)^2} - A_n e^{-((E+E_n)/\sigma)^2}, \quad (6)$$

and

$$\sigma = \frac{Br_n}{2\sqrt{\ln(2)}}, \quad (7)$$

and, finally,

$$\epsilon_{n1} = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\xi \epsilon_{n2}(\xi)}{\xi^2 - E^2} d\xi. \quad (8)$$

The three fitting parameters that are employed for the WVASE[®] fitting in this particular case are A_n , where the corresponding unit is dimensionless; E_n , where the unit is eV; and Br_n , where the unit is also eV.

Another ellipsometric model that will be employed in this analysis is the aforementioned BEMA model. This model makes the *self-consistent* choice of the *host material* complex dielectric function equal to the multi-component material's ultimate *effective* complex dielectric function. The BEMA model requires the numerical solution of the following expression for two constituents A and B, respectively:

$$f_A \frac{\tilde{\epsilon}_A - \tilde{\epsilon}}{\tilde{\epsilon}_A + 2\tilde{\epsilon}} + f_B \frac{\tilde{\epsilon}_B - \tilde{\epsilon}}{\tilde{\epsilon}_B + 2\tilde{\epsilon}} = 0. \quad (9)$$

For the glass substrate, the expression for the dielectric function is the following:

$$\epsilon_{n_pole} = \frac{A_n}{E_n^2 - E^2}. \quad (10)$$

It is the so-called pole or Sellmeier term, which corresponds to a Lorentz oscillator with zero broadening. Additionally, two *gaussian* oscillators will also be added in order to complete the accurate description of the Corning[®] transparent glass substrate used in the UV and IR frontiers.

It is worth pointing out that several studies have reported that the variation of the two optical constants n and k of a thin film along the normal direction to the film is most frequently due to the drifting of the deposition process parameters [28]. This fact suggests that the optical model with a one-dimensional graded index along the normal direction to the thin layer can reasonably be adopted in the present case. *Graded* layers work by introducing a series of homogeneous layers, whose optical constants slightly and gradually change in each of the successive layers.

Figure 5a displays a very detailed and realistic schematic of a Cu₃N thin film onto a bare transparent glass substrate. Figure 5b, on the other hand, is the suggested model to accurately fit the measured ψ and Δ parameters, where a BEMA model with 50% of air void is employed in order to provide an account for the effect of the existing Cu₃N rough surface; a one-dimensional graded index model throughout the whole film from bottom to top, combined with one T-L oscillator and up to four Gau oscillators, are employed in order to fully describe the three Cu₃N bulk flat layers under study. Finally, two zero-width oscillators and two additional Gau oscillators are chosen in order to accurately describe the Corning[®] glass transparent substrate employed in our RF magnetron sputtering depositions.

Next, we must first define a convenient statistical quantity that is called the *maximum likelihood* estimator. We will now elaborate a little bit more about this aspect by stating that the principle of maximum likelihood assumes that the population sample is a fair

representation of the whole population and selects a correct estimator that maximizes the probability density function (in continuous cases) or probability mass function (in discrete cases). This particular choice represents the level of accuracy in correctly matching the data obtained from the *constructed* optical model to our experimentally measured data [30]. It must be mentioned that the parameters of the particular oscillators were all appropriately varied in the process. This maximum likelihood estimator must be necessarily positive and must go down to zero (or, at least, go down to an *absolute* minimum) when the model-generated data *exactly* matches the experimentally measured data. The present Woollam WVASE software employs the following mean-square error (MSE) estimator:

$$\text{MSE} = \sqrt{\frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{\text{mod}} - \psi_i^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}} \right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}} \right)^2 \right]} = \sqrt{\frac{1}{2N - M} \chi^2}, \quad (11)$$

where N is the number of (ψ, Δ) ellipsometric angle pairs, M is the total number of *free* fitting parameters in the adopted optical model, and the introduced values of σ are the corresponding standard deviations associated with all of the collected and measured data points. Another very common estimator, the so-called *chi-square*, χ^2 , is introduced in Equation (11) for the sake of illustration.

The measured and simulated values of ψ and Δ at the three selected angles of incidence of 50° , 60° , and 70° , respectively, within the UV/Visible/NIR wavelength range from 300 up to 2200 nm, are depicted in Figure 6a–d. It can be clearly noticed that excellent fitting results were obtained for both ellipsometric parameters ψ and Δ . Through the optimization process carried out, it was found that the best fitting results were achieved with: (i) a graded index variation from bottom to top of approximately 5.0–14.0 % and (ii) thicknesses of the Cu_3N bulk layer and surface roughness layer, d_{bulk} and d_{rough} , of around 310 to 570 nm and close to 20 to 50 nm, respectively, with all of them being in close agreement with the estimated values from the independent SEM and AFM measurements (see Figure 2 and 3). Lastly, the calculated parameters belonging to the best fit for each Cu_3N sample and their experimentally measured values are all listed in Table 3. It has also been found that if either the adopted graded index model was *not* included or if all the oscillators were the fully chosen T-L oscillator, the associated fitting results were notably worsened, causing an incorrect derivation of the optical constants. Contrarily, if all of the oscillators adopted Gau oscillators, the resulting optical constants were only slightly affected in comparison with those presented in this work.

Next, we show that a measurable *depolarization* effect has clearly been observed in all of the specimens. Depolarization arises when effects that deviate from ideality come into play in ellipsometric measurements. To begin with, it must be said that depolarization does occur if the reflected beam contains multiple polarization states. In the case of *isotropic* samples—as we assume in our case of the Cu_3N thin layers—depolarization D can be calculated from the values of the two ellipsometric angles, ψ and Δ , respectively, as follows:

$$D = 1 - [(\cos 2\psi)^2 + (\sin 2\psi \cos \Delta)^2 + (\sin 2\psi \sin \Delta)^2]. \quad (12)$$

The depolarization spectra of the Cu_3N samples were measured by also employing the Woollam VASE ellipsometer in the spectral range of 300–2200 nm; some of these spectra are shown in Figure 6e. Evaluation of the depolarization spectra was also carried out using the WVASE software.

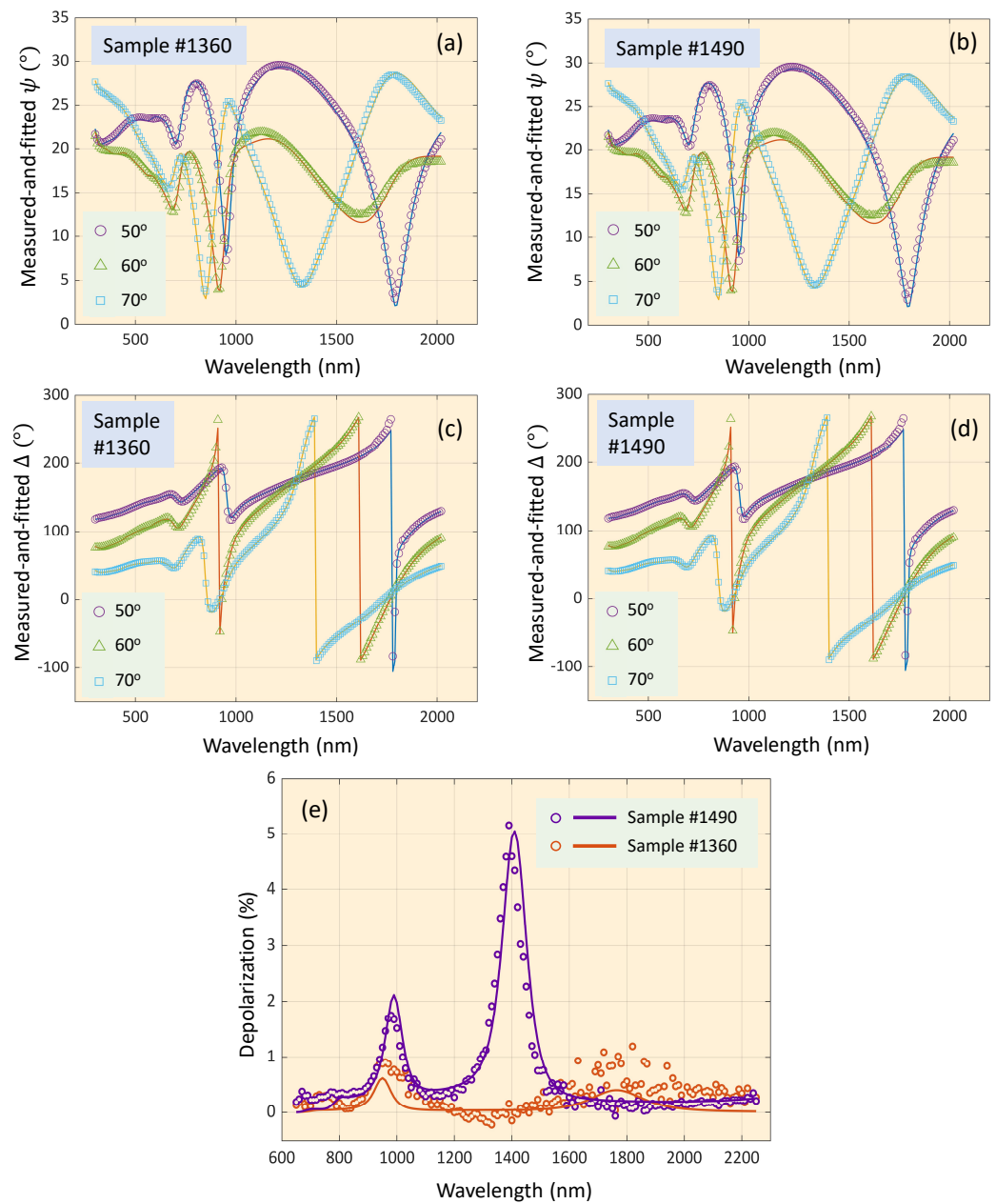


Figure 6. (a,b) The measured and fitted ψ values at the three angles of incidence of 50°, 60°, and 70° in the wavelength range from 300 nm up to 2200 nm. (c,d) The measured and fitted Δ values at the same previous angles and in the same previous experimental spectral range. (e) Depolarization spectra of the two representative copper nitride thin films at the angle of incidence of 60°. The curve fitted by employing the ellipsometric method is described in-depth in the text; it is also presented using a solid line. The depolarization has been modeled with 2.3% and 5.2% thickness non-uniformity in the cases of sample #1360 and #1490, respectively.

5. Results and Discussion

5.1. Complex Index of Refraction and Dielectric Function

By using the previous best-fitting results, we can find the corresponding *dispersive* n and k values. They are displayed in Figure 7, and it must be emphasized that we extended our values of the complex refractive index $\tilde{n} = n - ik$ up to the NIR wavelength of 2200 nm; it represents an excellent opportunity to perform useful designs and simulations on high-efficiency solar cells. To additionally confirm the correctness of ellipsometrically calculated

optical constants, the independent comparison of the measured and predicted values of the normal incidence transmission in the wavelength range under study is shown in Figure 7. We have *calculated* the normal incidence transmission exclusively based on the results found from the ellipsometric analysis. For this purpose, we have carefully tried to carry out all of the measurements on the very same spot of each thin film sample. The difference observed between the predicted and experimental values of transmittance were mainly due to the unavoidable differences in the positions on the sample and due to the experimental uncertainty of the transmission intensity measurements that were performed by the Woollam single-beam VASE ellipsometer. However, it can be observed that an outstanding agreement between the experimentally measured and calculated transmission spectra was reached in our samples; thus, it provides extra confidence upon the n and k that were exclusively determined from the VASE measurements in the spectral range from 300 up 2200 nm. Moreover, it is worth pointing out that the color of our semi-transparent Cu_3N thin films is reddish dark brown, or mahogany red (see the respective insets in Figure 8, which shows the visual appearance of the three specimens). The differences in color of the investigated Cu_3N samples are obviously a direct consequence of their measured transmission spectra, as shown in Figure 8.

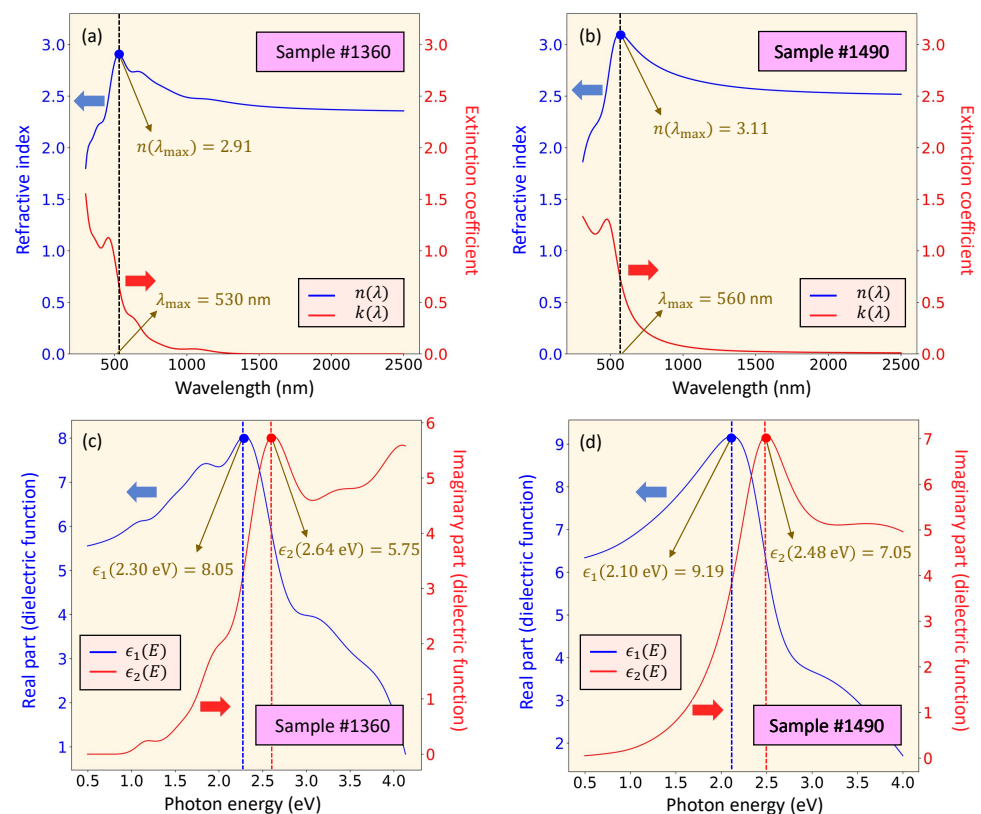


Figure 7. (a) Real part of the complex refractive index, n , and (b) imaginary part of the complex refractive index, k , of the Cu_3N thin layers. (c) The real, ϵ_1 , and (d) imaginary ϵ_2 , parts of the complex dielectric function.

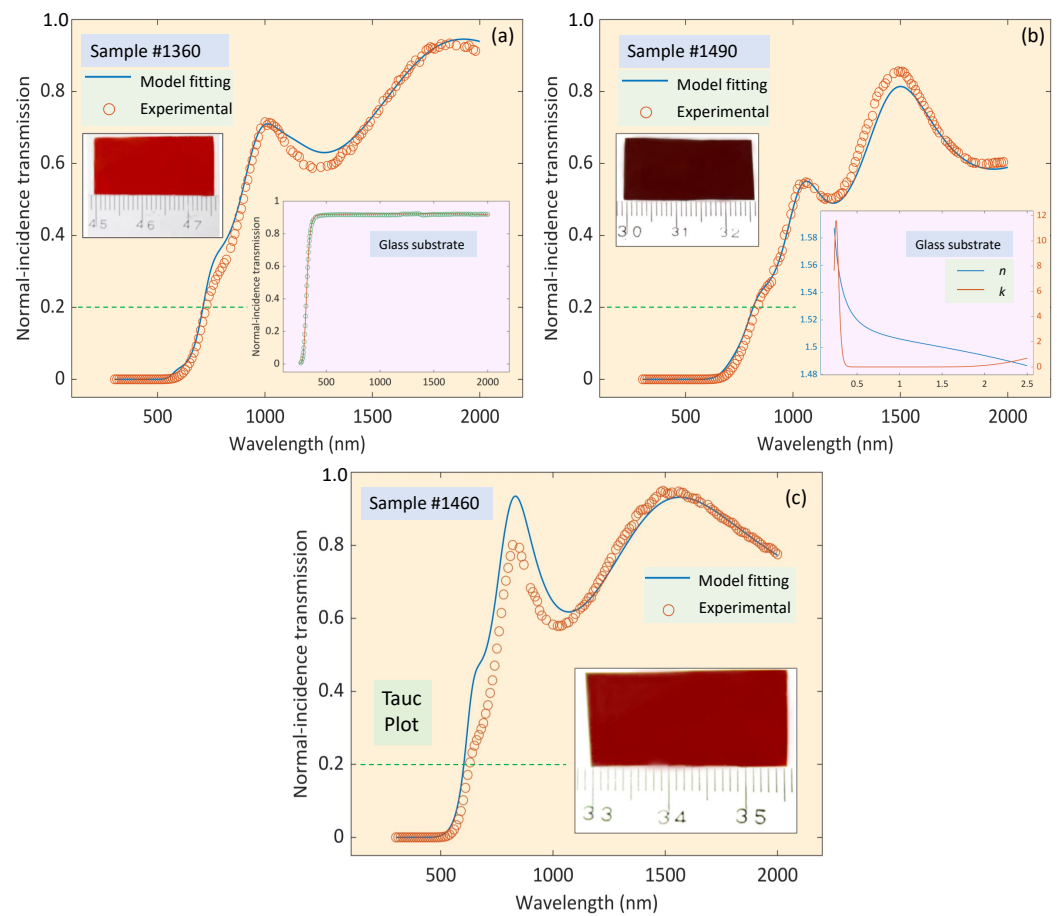


Figure 8. Experimentally measured optical transmission intensity data, acquired by using the varied angle spectroscopic ellipsometer and the computationally predicted values of transmittance in the studied spectral range: (a) sample #1360, (b) sample #1490, and (c) sample #1460.

Let us now discuss the *optical dispersion*, or chromatic dispersion, which is an important parameter for more deeply understanding the optical properties of quasi-transparent (weakly-absorbing) Cu_3N films. Optical dispersion is the required parameter in order to quantify the change in the material's refractive index with respect to the incident light wavelength $dn/d\lambda$. Typically, in non-absorbing materials, the real refractive index increases with incident light frequency; that is, $dn/d\lambda < 0$ in the *normal* dispersion regimen. In the opposite case, where $dn/d\lambda > 0$, we are in the *anomalous dispersion* regimen; that is, increasing the light frequency results in a decrease in the real index of refraction. In our RF-sputtered Cu_3N samples, the values of the vacuum light wavelength where the transition takes place (the so-called refractive index threshold wavelength), i.e., where $dn/d\lambda = 0$, are 530 nm and 560 nm for the two representative samples #1360 and #1490, respectively (see Figure 7a,b).

The real and imaginary parts of the complex dielectric function ϵ_1 and ϵ_2 , on the other hand, are obtained as a function of the refractive index n and extinction coefficient k , respectively, which are obtained from the fundamental expressions (based upon the basic relationship, $\tilde{\epsilon} = \tilde{n}^2$):

$$\begin{aligned}\epsilon_1 &= n^2 - k^2, \\ \epsilon_2 &= 2nk.\end{aligned}\tag{13}$$

Concerning the obtained shape of the real and imaginary parts of the complex dielectric function upon the photon energy (see Figure 7c,d), as is typical for a semiconductor or insulator material, it certainly agrees well with the previously reported data [4]. However,

in our particular Cu₃N specimens, the magnitude of the peaks of ϵ_1 and ϵ_2 of about 8.0 and 6.0, respectively, is a multiplying factor of around 1.5 and 2.0 smaller than the values reported in [4], respectively (all of them being one order of magnitude thinner than our Cu₃N films and with an optical gap of 1.65 eV). These results could be an effect that is strongly correlated with the values of the film thickness, which was much thicker in our presently prepared Cu₃N layers.

5.2. Additional Calculation of the Indirect and Direct Tauc Gap and Urbach Energy

At this point in the paper, it must be stressed that each semiconductor material has *both* direct and indirect gaps; whichever is lower shall determine the specific nature of its energy band gap. It must be remembered that the band gap is a property that is basically associated with the *lattice constant* of the material; in fact, its band gap can readily be changed by varying the value of its lattice constant. This particular value can be changed by various ways, e.g., by applying pressure, by heating or cooling, or by mixing with another semiconductor material. Both the direct and indirect band gaps will be modified with the change of the lattice constant, but at different rates.

Regarding the calculation of the energy band gap of the investigated Cu₃N thin layer material, it should be recalled that while investigating the electronic properties of *a*-Ge, Tauc et al. [31] proposed a nowadays well-established method for determining the band gap by using optical data that is plotted conveniently versus photon energy. The optical absorption strength depends upon the difference between the photon energy and the band gap, and it is expressed by the following relation:

$$(\alpha\hbar\omega)^{1/m} = A(\hbar\omega - E_g), \quad (14)$$

where $\hbar$ is the Dirac's constant, α ($= 4\pi k/\lambda$) is the absorption coefficient, E_g is the band gap, and A is a proportionality constant (energy-independent), also called the band tailing parameter; A is actually a function of the refractive index of the material and its carrier effective mass. The value of the exponent denotes the actual nature of the corresponding electronic transition, whether it be *allowed* or *forbidden* and whether it be *direct* or *indirect*:

- (i) Direct and allowed transitions, $m = 1/2$;
- (ii) Direct and forbidden transitions, $m = 3/2$;
- (iii) Indirect and allowed transitions, $m = 2$;
- (iv) Indirect and forbidden transitions, $m = 3$.

Usually, the allowed transitions clearly dominate the basic optical absorption processes, giving either $m = 1/2$ or $m = 2$ for direct and indirect electronic transitions, respectively. Hence, the main procedure for a "Tauc analysis" is to accurately determine the optical absorption coefficient data that spans a photon energy range from below the band gap transition to above the transition. Thus, plotting $(\alpha\hbar\omega)^{1/m}$ against $\hbar\omega$ is a way of testing either $m = 1/2$ or $m = 2$ in order to compare which provides the better fit, thus identifying the correct electronic transition type. We will next experimentally find that the smaller value of the indirect band gap is, as expected, accompanied by the larger spectral range of agreement in the fit in its corresponding "Tauc-extrapolation plot". It must be emphasized that the calculated value of the *indirect* band gap for our Cu₃N layers is well within the *optimal* band gap range for solar cell applications, which is approximately 1.4–1.5 eV.

The indirect band gap was obtained by plotting the $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ curve and by extrapolating the full line to the abscissa of $\hbar\omega$ (see Figure 9). Similarly, the direct band gap was found by extrapolating the full line to the abscissa of $\hbar\omega$ in the $(\alpha\hbar\omega)^2$ versus $\hbar\omega$ curve (see again Figure 9). The direct and indirect band gap values for the two representative Cu₃N specimens #1360 and #1490 were found to be 1.45 and 1.46 eV, respectively, and 2.21 and 2.14 eV, respectively. The alternate calculation of the indirect and direct band gap by using UV/visible/NIR normal incidence transmission measurements gave rise to practically the same values as those shown in Figure 9. This is explained by the fact that the

simulated transmission almost coincides with the experimentally measured transmission up to the value of transmission of about 0.20 (see Figure 8).

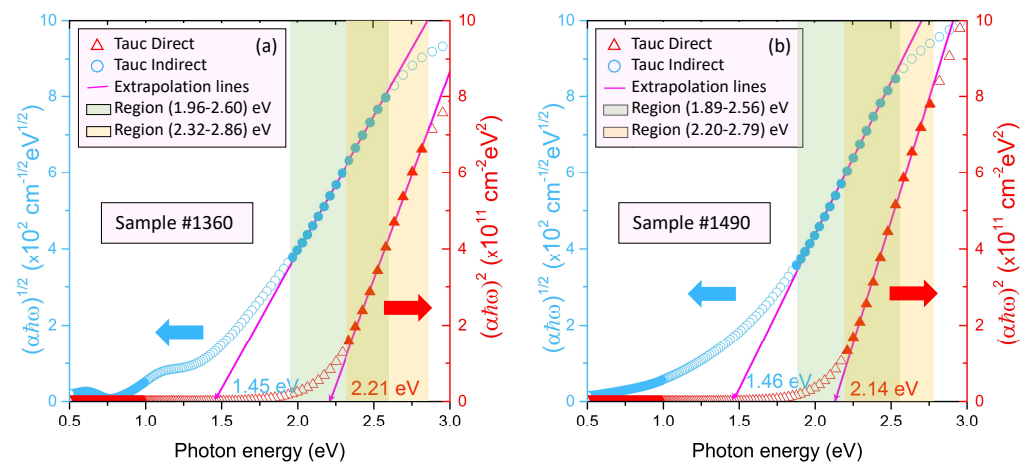


Figure 9. $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ plot for the determination of the *indirect* energy band gap and $(\alpha\hbar\omega)^2$ versus $\hbar\omega$ plot for the calculation of the *direct* energy band gap, presented for the samples (a) #1360 and (b) #1490, respectively.

It must now be mentioned that there is generally highly inconsistent and discrepant information about the optical properties of Cu_3N layers; those optical properties of Cu_3N have been the subject of strong controversy with respect to the bulk band gap values as well as the precise nature of its electronic transitions. The band gap values are found to widely vary between 0.23 eV and 2.38 eV, and the concrete nature of the band gap transition has paradoxically been reported to be *both* direct as well as indirect.

Going even more deeply into the optical properties of the Cu_3N thin films, it is well-known that the structural disorder in a material gives rise to a tailing of the density of states in the forbidden energy gap, the so-called Urbach tail, and that the width of the tail is the Urbach energy E_u . In this way, a higher value of E_u means a lower degree of structural order. The absorption coefficient α is linked to the structural order parameter E_u by the following expression [32–36]:

$$\alpha = \alpha_0 \exp\left(\frac{\hbar\omega}{E_u}\right), \quad (15)$$

where α_0 is a constant; the structural parameter E_u is therefore obtained from the linear fitting of the semilogarithmic graph of α versus $\hbar\omega$ (see Figure 10, where the *optical absorption edge* is shown). Specifically, the inverse of the slope provides the value of the parameter E_u : The value is found to be 96 meV in the particular case of specimen #1360, 242 meV in the particular case of specimen #1490, and 170 meV for specimen #1460 (see Table 3 and Figure 10). From these values of E_u , it is inferred that in the first of the three Cu_3N samples, with a different gaseous environment of $\text{N}_2 + \text{Ar}$, the degree of *structural disorder* is notably smaller than in the other two samples, with a gaseous environment of just N_2 .

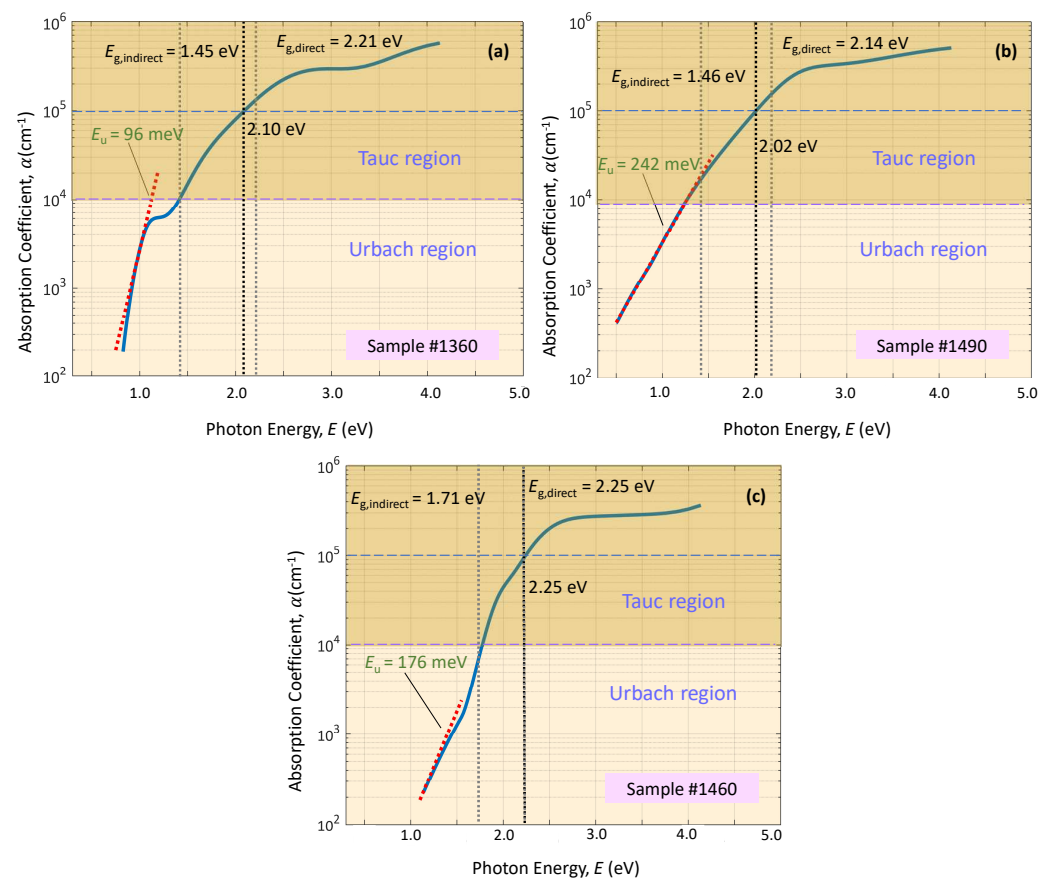


Figure 10. A semilogarithmic plot of the absorption coefficient as a function of incident photon energy for copper nitride thin films grown on glass substrates. The exponential dependence is valid in the near band-edge region. The slope of the linear fit is used to calculate the Urbach-energy parameter, E_u : (a) sample #1360, (b) sample #1490, and (c) sample #1460.

Moreover, these previous values of E_u are indeed comparable to those reported by other authors in the case of Cu_3N thin films, which allows us to interpret this Urbach energy as the bandwidth of the electronic states located within the band gap width. That is, the Urbach tail is associated with the density of *localized* electronic states. In other words, the calculated value of E_u is an excellent indicator of the level of structural *defects* existing in the atomic structure of the semiconducting material under study.

Concerning the electronic properties of our material under investigation, it ought to be indicated that the calculated energy band structure of Cu_3N shows that it is undoubtedly a semiconductor at ambient pressure [26]. Specifically, the Cu orbitals dominate the conduction bands at the R and M points of the *first Brillouin zone* (see all of the details shown in the inset of Figure 1c), and the valence band consist of a $2p$ orbital of N atoms for the same symmetric points. From the partial density of states, strong hybridization has been observed between the N and Cu states, which is mainly related to both the N $2p$ and Cu $3d$ orbitals, respectively. The maximum valence band is at the R point of the first Brillouin zone, and the minimum conduction band is at the M point. It was finally concluded that the initial potential transition is the one between the highest occupied state at the R point and the lowest unoccupied state at the M point when all direct and indirect electron transitions were taken into account. This unambiguously shows that Cu_3N is an *indirect band-gap* semiconducting material, as has clearly been corroborated in our work.

6. Conclusions

- (i) In the present investigation, polycrystalline Cu₃N thin films were deposited by making use of reactive RF magnetron sputtering at room temperature using a total pressure of 5.0 Pa, RF power of 50 W, and *two* different gaseous environments of N₂ and N₂ + Ar, respectively. The film thicknesses ranged between 330 and 610 nm. The XRD patterns showed that the Cu₃N thin films exhibited an *anti*-ReO₃ structure. In order to enrich the depth of the analysis of the semiconductor material, AFM, SEM (by using FIB sample preparation), and EDX measurements were systematically performed in all of the RF-sputtered thin layers. The results of the SEM and AFM microscopy demonstrated the film's consistency with a desired surface morphology.
- (ii) The complex refractive index of the RF-sputtered Cu₃N thin films was accurately determined via VASE measurements at three angles of incidence: 50°, 60°, and 70°. The constructed ellipsometric model consisted of a one-dimensional graded index plus a BEMA model with a 50% air void in order to describe both the bulk Cu₃N layer and the rough surface. The experimentally measured normal incidence transmission spectrum and the predicted transmission spectrum based upon the obtained ellipsometric results showed reasonably good agreement in all cases. The calculated optical constants allowed us to design and simulate a potential photovoltaic electronic device. The absorption strength, on the other hand, reached a magnitude of $1.0 \times 10^5 \text{ cm}^{-1}$ from approximately 2.0 eV, suggesting a very promising potential for solar cell-based applications. The lower Urbach energy value for the case of the sample #1360 with a gaseous environment of N₂ + Ar is associated with the presence of a much lower level of defects in its atomic structure compared with the samples of a gaseous environment of just N₂.
- (iii) Last but not the least, the investigated Cu₃N material with the corresponding values of E_g in the energy range of 1.45–1.71 eV can unambiguously be considered as satisfactory for use as a solar light absorber material. The specific aspect of the solar cell technology that could certainly benefit the most from the use of the Cu₃N thin film material would be that which is related to the photovoltaic electronic devices, as the material provides a flexible texture and is relatively *inexpensive* to manufacture.

In this sense, any practical applications of copper nitride shall be mainly conditioned by the size of its optical band gap. This binary compound will undoubtedly serve as a springboard for upcoming study fields that will have an influence on transition metal nitride material science. We will continue our research in the near future by using infrared spectroscopic ellipsometry analyses to examine down to the middle infrared spectral region.

Author Contributions: Conceptualization and methodology: E.M., M.B. and M.G.-G.; software: M.C.P., M.B. and M.G.-G.; visualization: S.M.R. and M.R.T.; Measurements: M.D.d.l.V., J.M.M. and E.B.; writing (original draft preparation): E.M.; reviewing and editing: E.M., M.B. and M.G.-G.; supervision: E.M.; funding acquisitions: E.M., S.M.F. and M.I.R.-T. All authors analyzed the results. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by MCIN/AEI/10.13039/501100011033, grant number PID2019-109215RB-C42. M.A. Rodríguez-Tapiador acknowledges partial funding through MEDIDA C17.I2G: CIEMAT. Nuevas tecnologías renovables híbridadas, Ministerio de Ciencia e Innovación, Componente 17 “Reforma Institucional y Fortalecimiento de las Capacidades del Sistema Nacional de Ciencia e Innovación”. Medidas del plan de inversiones y reformas para la recuperación económica funded by the European Union—NextGenerationEU. M.D.de la V. also acknowledges the financial support from the Spanish Ministerio de Ciencia e Innovación, under the project reference EQC 2018–004704-P FEDER 2014–2020.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: J.M.M. would like to acknowledge the SC-ICYT of the University of Cádiz, and Dra. L. González-Souto for the received assistance.

Conflicts of Interest: The authors declare no conflict of interest.

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