

Power effect on the properties of copper nitride films as solar absorber deposited in pure nitrogen atmosphere

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Abstract

Nowadays, the copper nitride (Cu_3N) is of great interest as a new solar absorber material, flexible and lightweight thin film solar cells. This material is a metastable semiconductor, non-toxic, composed of earth-abundant elements, and its band gap energy can be easily tunable in the range 1.4 to 1.8 eV. For this reason, it has been proposed for many applications in the solar energy conversion field. The main aim of this work is to evaluate the properties of the Cu_3N thin films fabricated by reactive radio-frequency (RF) magnetron sputtering at different RF power values to determine its potential as light absorber. The Cu_3N films were fabricated at room temperature (RT) from a Cu metallic target at the RF power ranged from 25 to 200 W on different substrates (silicon and glass). The pure nitrogen flux was set to 20 sccm, and the working pressures were set to 3.5 Pa and 5 Pa. The XRD results showed a transition from (100) to (111) preferred orientations when RF power increased; the AFM images revealed a granular morphology, while FTIR and Raman spectra exhibited the characteristics peaks related to Cu-N bonds, which became narrower when the RF power increased. Finally, to establish the suitability of these films as absorber, the band gap energy was calculated from transmission spectra.

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Abstract

Nowadays, the copper nitride (Cu_3N) is of great interest as a new solar absorber material, flexible and lightweight thin film solar cells. This material is a metastable semiconductor, non-toxic, composed of earth-abundant elements, and its band gap energy can be easily tunable in the range 1.4 to 1.8 eV. For this reason, it has been proposed for many applications in the solar energy conversion field. The main aim of this work is to evaluate the properties of the Cu_3N thin films fabricated by reactive radio-frequency (RF) magnetron

sputtering at different RF power values to determine its potential as light absorber. The Cu_3N films were fabricated at room temperature (RT) from a Cu metallic target at the RF power ranged from 25 to 200 W on different substrates (silicon and glass). The pure nitrogen flux was set to 20 sccm, and the working pressures were set to 3.5 Pa and 5 Pa. The XRD results showed a transition from (100) to (111) preferred orientations when RF power increased; the AFM images revealed a granular morphology, while FTIR and Raman spectra exhibited the characteristics peaks related to Cu-N bonds, which became narrower when the RF power increased. Finally, to establish the suitability of these films as absorber, the band gap energy was calculated from transmission spectra.

Keywords: Copper nitride, reactive magnetron sputtering, pure nitrogen atmosphere, absorber, photovoltaic devices.

Introduction

The Cu_3N is of great interest as a new solar absorber material, flexible and lightweight thin film solar cells [1, 2]. This increasing interest as absorber for photovoltaic (PV) applications is due to the fact that is a metastable, non-toxic semiconductor, composed of earth-abundant elements, and its band gap energy can be easily tunable in the range 1.4 to 1.8 eV [3]. These values mean that the Cu_3N film can be considered as a possible substitute for the conventional silicon. Furthermore, this material can show both n and p-type character, which can be obtained by doping it with different elements that placed in interstitial position, such as fluorine [3].

Cu_3N is a metastable semiconductor with an anti- ReO_3 cubic crystal structure[3]. The structure exhibits nitrogen (N) atoms at the corners of the cube and copper (Cu) atoms in the middle of each edge. The material is thermally and structurally stable at temperatures up to 200°C [4]. However, its thermal decomposition occurs in the temperature range of 100–470 °C [5]. In this sense, it has been reported that at high temperatures, visible structural changes can be appreciated and they may be related to the release of pure Cu [6].

The Cu-N family of bonding compounds can offer different optoelectronic properties, i.e. Cu_4N that shows metallic behaviour, while Cu_3N presents a semiconductor one, where there is a strong relationship between its chemical bonds and its electronic properties. These different behaviours can be achieved depending on the fabrication technique employed and modifying the deposition conditions. Such different behaviours are basically attributed to the vacant interstitial sites, because Cu atoms do not occupy the face-centered cubic (FCC) close packing sites[7]. Thanks to this, it is possible to tune the optoelectronic properties by incorporating different atoms in such vacant sites. In addition, the films can show different properties depending on the technique used. Among the main methods used for the Cu_3N deposition, we can find molecular beam epitaxy (MBE) [8], pulsed magnetron sputtering (PMS) [9], pulsed laser deposition (RPLD) [10], and reactive direct current (DC) magnetron sputtering [11] or reactive radio-frequency (RF) magnetron sputtering [12-15]. In this last case, the film stoichiometry and the properties can be easily changed. This can be achieved by modifying the main deposition parameters: (i) the gas pressure due to the interaction between N and Cu that could modify the band gap [6], (ii) the substrate temperature and the power that can affect the structural, electrical and optical properties of the films [16], (iii) the type of the substrate [13], and (iv) the substrate to target distance [8]. Among these parameters, the plasma gas composition and the gas pressure control the N fraction in the gas mixture, which has a strong impact on the film structure, i.e. the lattice constant ranged from 0.3815 to 0.3885 nm, and consequently, on their optoelectronic properties [17].

In view of the above, in this work we evaluate the effect of the RF power on the structural and optoelectronic properties of Cu_3N thin films sputtered at room temperature (RT) in a pure N atmosphere, without introducing argon, to obtain a suitable material for being used as light absorber. It is expected to determine the optimized RF values to achieve the Cu_3N films with appropriated morphologies, structures and band gap energies suitable for the chosen application.

Materials and Methods

The deposition of the Cu_3N thin films were carried out with a commercial MVSystem INC. monochamber sputtering system, where there is only one gun that can be vertically adjustable and is RF operated. The target used is a pure commercial Cu target (99.99%) with a 3-inch diameter, from Lesker Company. In this work, we used two types of substrates: 1737 Corning glass (Corning Inc., New York, USA) and $\langle 100 \rangle$ polished n-type floating zone crystalline silicon (c-Si) wafers. Prior to be loaded into the sputtering chamber, both substrates were prepared in a different way. The native silicon dioxide on the surface silicon wafer is removed with a 1% HF solution in deionized water and ethanol for 5 minutes. In the case of the glass, it was cleaned for 10 minutes in ultrasound, with ethanol and deionized water, and finally immersed in isopropyl alcohol. Subsequently, the substrates were dried by blowing nitrogen over them. After loading the substrates, the chamber was pumped to a pressure of 10^{-5} Pa. The working pressure was set to 3.5 and 5.0 Pa, adjusting it with a “butterfly” valve. The process gas was pure N_2 (purity 99.999%) at a flow rate of 20 sccm, controlled by a mass flow controller (MFC). The distance between the target and the substrate was set to 10 cm. Cu_3N thin film depositions were performed at different powers ranged from 25 to 200W, and the deposition time was modified from 420 to 1800 s, depending the RF power value, to counteract the effect of the power on deposition rate.

The structure of the thin film was determined by X-ray diffraction (XRD), using a commercial Panalytical powder diffractometer model X’Pert MPD/MRD, with a Cu anode and secondary monochromator. The radiation used was Cu- $\text{k}\alpha$ radiation ($\lambda=0.15406\text{nm}$), and the scanned 2θ range was 10° - 60° at a step size of 0.01° . To determine the chemical composition and molecular structure, Raman and Fourier transform infrared spectroscopy (FTIR) were used. Raman measurements were carried out with the dispersive spectrometer Horiba Jobin-Yvon LabRam HR 800 coupled, to an optical microscope Olympus BXFM, using a solid-state laser as an excitation source emitting at 532 nm. The Raman spectra were obtained with a laser power at the sample of about 5 mW and using a $100\times$ microscope objectives. FT-IR measurements were carried out with a Perkin Elmer Spectrum 100 FT-IR in range of 400 - 4000 cm^{-1} . The morphology of the films was studied by atomic force microscopy (AFM) using an AFM model III A multimode nanoscope (Bruker). The roughness of the samples was determined from the root mean square (RMS) calculated with the commercial Gwyddion software. Finally, the optical properties were calculated from the transmittance spectra in the range 300 - 2000 nm , measured at RT and normal incidence with a Perkin Elmer Lambda 1050 spectrophotometer.

Results and discussion

Figure 1 shows the XRD spectra of the Cu_3N films deposited on glass at different RF powers and at the different working pressures of 3.5 and 5.0 Pa. Regardless the pressure used, the XRD patterns show Cu_3N crystallites with an anti- ReO_3 structure [18]. The Cu_3N films deposited at low RF power values (below 150 W) present as preferential orientation the (100) plane that corresponds to the N-rich planes. As the RF power increases above 100 W, the intensity of the main (100) diffraction peak begins to decrease, while the (111) diffraction peak, corresponding to a Cu-rich plane, starts to appear as preferred from the sample deposited at 150 W [5]. In addition, this sample also presents several diffraction peaks of weaker intensity such as the (110) and (210) planes, referenced from the XRD card number 00-047-1088 (The Joint Committee on Powder Diffraction Standards, 47–1088). This change observed in the phase transition orientation from the preferred (100) plane to the (111) one as the RF power increases can be attributed to the presence of a larger number of Cu atoms in the plasma. The high presence of Cu atoms could cause the formation of a Cu_3N material saturated with Cu, which retains a cubic structure that begins to disappear and/or change at very high RF powers.

On the other hand, the main effect that the total pressure exerts on the films is the amorphous character, observed in the sample deposited at the highest pressure and the highest RF power of 200 W. Upon increasing the deposition pressure from 3.5 Pa to 5.0 Pa produces more N ions, are bombarding the Cu target, leading to a higher amount of Cu ions or atoms in the plasma, with the Cu^{2+} and Cu^+ ionization states. The sample deposited at 200 W and 5.0 Pa shows amorphous structure, in comparison with that deposited at 200 W and 3.5 Pa. This can be attributed to a high presence of Cu atoms, because of the high RF power, that would reach the substrate surface with less energy due to the increase of the collisions between the particles

within the plasma at the increased pressure. The saturation effect of the Cu in the film at higher pressures is more evident. This is the reason why the Cu-rich phase disappears. In addition, under these extreme conditions, there is an increase in ion bombardment, resulting in more defects produced in the sputtered films. This indicates that the crystallinity of the film is seriously deteriorated due to the excessive RF power and subsequently, excessive amount of Cu atoms.

Conversely, at low RF power values, more N^{+2} and N^+ free radicals are generated due to the high proportion of low-energy electrons that are formed in the plasma[15]. Hence, the samples deposited at low RF powers show the preferential N-rich planes, and a better crystal quality.

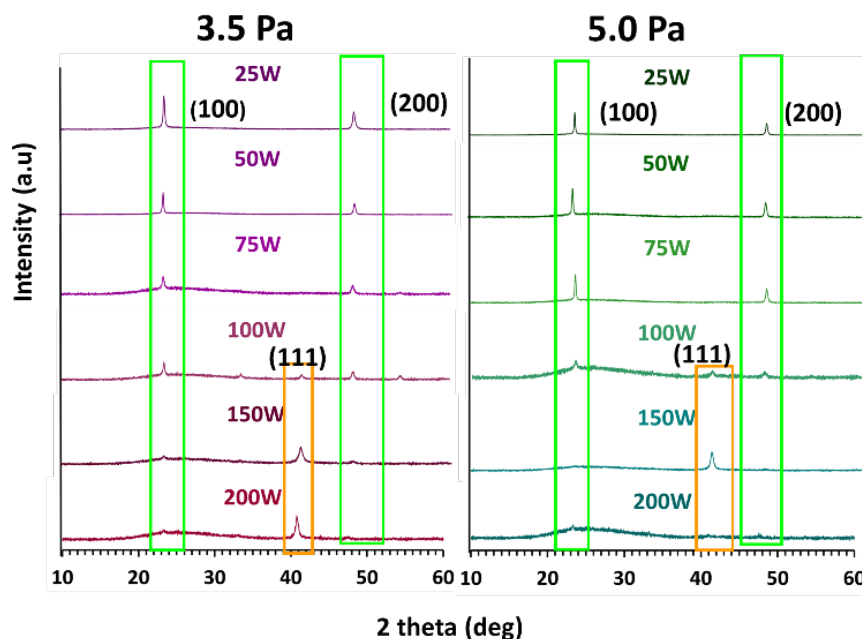


Figure 1. X-ray diffraction pattern of Cu_3N films deposited at different RF Power and the working pressure of 3.5 Pa (left) and 5.0 Pa (right).

The stoichiometry of Cu_3N is studied in the films deposited on silicon by using FTIR and Raman techniques. These two techniques give information on the vibrational state of the molecular bonds that are found in the films. Both techniques are considered as complementary. As shown the Figure 2 and Figure 3, the FTIR and Raman peaks reveal the formation of Cu_3N . The Figure 2 shows the FTIR spectra of the films as function of the RF power values, where a band around the wavenumber of 650 cm^{-1} was observed, being the typical peak of the stretching vibrations attributed to Cu-N bonds. The peaks at 5.0 Pa are wider than the ones obtained at 3.5 Pa and closer to 650 cm^{-1} ; while the band of the samples deposited at 150 and 200 W is quite far from the 650 cm^{-1} , revealing the change in their structure. On the other hand, the Figure 3 depicts the Raman spectra where the typical bands of Cu_3N thin films, found at the wavelength of 634 cm^{-1} [19], are the characteristic ones of Cu-N bonds [20]. A slight shift to lower wavenumbers is observed when the RF power increases, attributed to deviation from the stoichiometric level more evident at high RF powers where the Cu_3N structure is Cu-rich [21]. Whereas, the sample deposited at 200 W and 5.0 Pa presents a Raman spectrum completely different, which can be attributed to the appearance of CO_2 and/or CO absorption bands [22].

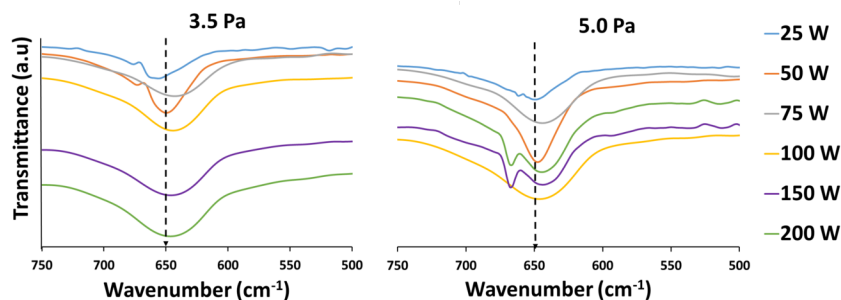


Figure 2. FTIR spectra of Cu_3N films prepared by magnetron sputtering at different RF power and the working pressures of 3.5 Pa and 5.0 Pa.

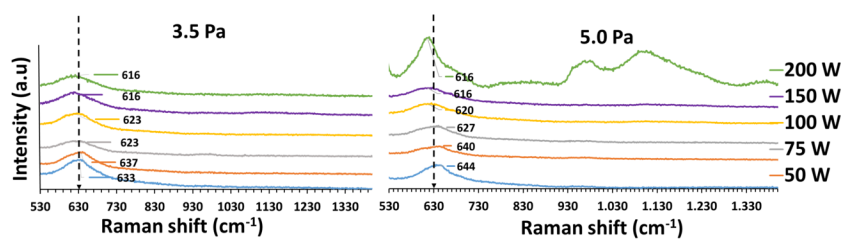


Figure 3. The Raman spectra of Cu_3N films prepared by magnetron sputtering at different RF power and the working pressures of 3.5 Pa and 5.0 Pa.

The surface of the samples was analysed by AFM. The scanning area was $1 \times 1 \mu\text{m}^2$. Figure 4 shows the surface roughness obtained from the root-mean-square (rms) as function of the RF power. As it can be observed, the higher the rms value, the rougher the surface of the thin film. It was also observed that the smoothest films with close-grained surface morphology were the surface of the samples made at 5.0 Pa and lower RF power values.

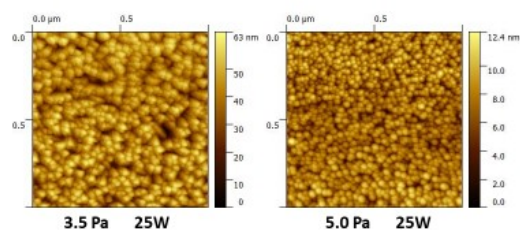
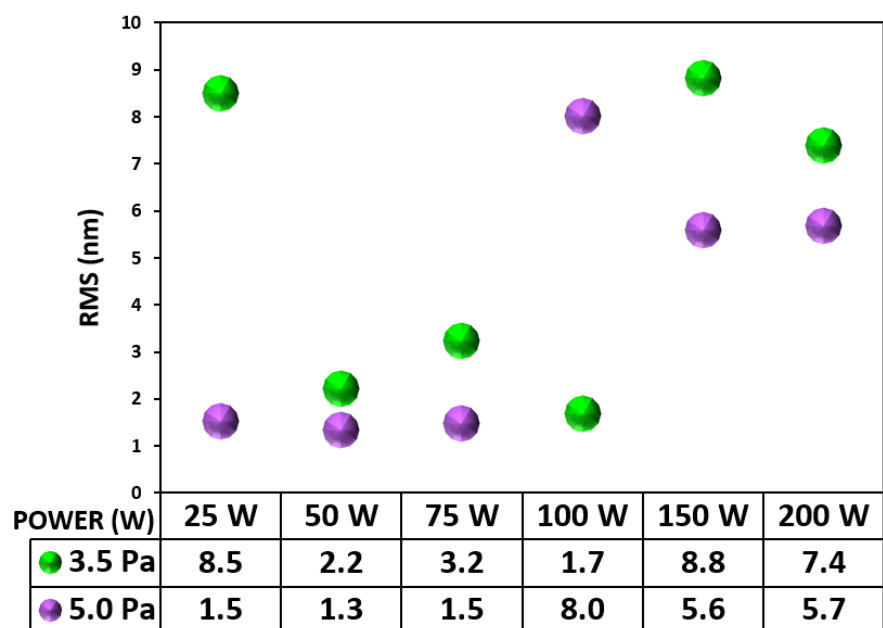
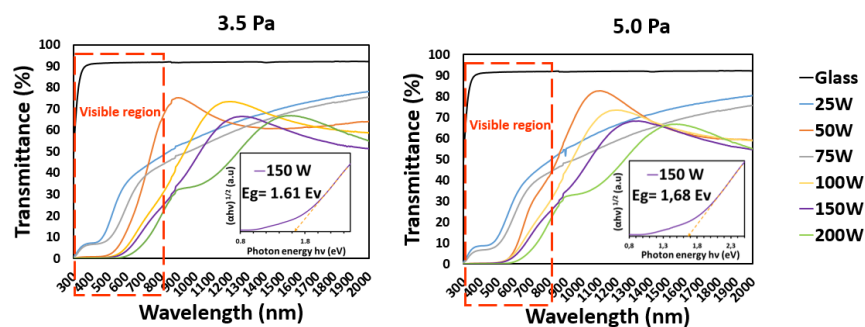


Figure 4. Rms values (nm) calculated vs RF power at different working pressures of 3.5 Pa and 5.0 Pa.



Finally, the optical properties of Cu₃N thin films deposited on glass substrates were analysed by UV-VIS-NIR spectroscopy in the range of 300-2000nm. Figure 5 pictures the transmittance spectra of the deposited thin films at 3.5 Pa and 5.0 Pa, where a greater number of fringes appear as RF power increases, attributed to the thicker films obtained by increasing the deposition rate with the RF power. These spectra clearly show a low transparency of the films in the visible region, and a maximum optical transmission close to 80%, showed for the samples deposited at low values of RF power, in the near infrared region.

Figure 5. Transmittance spectra of the Cu₃N in study. In the inset, representative $(h\nu\alpha)^2$ and $(h\nu\alpha)^{1/2}$ vs $h\nu$ plots of the sample deposited at 150 W, for the determination of the direct and indirect band gap.

From the transmittance spectra and the Tauc equation [23], the band gap of the Cu₃N films were calculated, with the aim of determining their potential as solar absorbers.

$$(\eta\nu\alpha)^{\frac{1}{p}} = A(h\nu - E_g) \text{Eq.1}$$

where A is the band tailing parameter and p is the parameter associated with type of transition, i.e. p=2 for an indirect allowed transition and p=1/2 is direct allowed transition, α is the absorption coefficient, and $h\nu$ is photon energy. In the inset of Figure 5, the $(h\nu\alpha)^2$ and $(h\nu\alpha)^{1/2}$ vs $h\nu$ plots for the sample deposited at 150 W are pictured as example. Table 1 summarised the values of the direct and indirect band energies obtained varying the RF power. They are very close to those found in the literature [9, 23]. In the case of the samples deposited at 3.5 Pa, we observe a slightly blue-shift in the band gap energy as the RF power increases. This may be attributed to the increasing presence of unbonded Cu atoms, which would form a defect level, leading to a reduction in the band gap. We would be faced with the effect of Cu supersaturation. However, in the case of the samples deposited at 5.0 Pa, that tendency is not so well appreciated. This leads us to believe that the Cu oversaturation effect would not be occurring due to the increase of the gas pressure [24].

Table 1. Direct and indirect band gap calculated by using Tauc plot for the samples deposited at different RF powers and a total pressure of 3.5 Pa and 5.0 Pa, respectively.

3.5 Pa						
RF Power (W)	25	50	75	100	150	200
Band Gap E_g (eV)						
$\Delta i r e c t (\alpha h \nu)^2$	2.16	2.12	2.04	2.08	2.04	2.04
$I n d i r e c t (\alpha h \nu)^{1/2}$	1.90	1.80	1.70	1.76	1.61	1.68

5.0 Pa						
RF Power (W)	25	50	75	100	150	200
Band Gap E_g (eV)						
$\Delta i r e c t (\alpha h \nu)^2$	2.12	2.12	2.04	2.04	2.04	2.04
$I n d i r e c t (\alpha h \nu)^{1/2}$	1.68	1.80	1.68	1.68	1.68	1.72

Conclusions

This work presents the optimization of the sputtering deposition of Cu₃N thin films using a N₂ pure environment, at RT and at different RF power values with the aim to determine its suitability as optical absorber. XRD patterns reveal a change in the preferred orientation from (100) to (111) as increasing the RF power. Moreover, at RF power of 100 W and above, a polycrystalline structure with the presence of several weak diffraction peaks are obtained. From the chemical point of view, FTIR and Raman measurements confirmed the presence of Cu-N bonds. From AFM images, it is observed that thin films prepared at low RF power and 3.5 Pa show very smooth surfaces. Finally, the direct and indirect band gap values calculated are suitable

for solar absorbers. Hence, these results indicate that (i) the magnetron sputtering is an appropriate method to fabricate this kind of material, and (ii) the depositions at low RF power (up to 100 W) and N_2 pressures of 3.5 Pa are mainly preferred due to its smoother surfaces, its stoichiometry closer to the required one, and suitable band gap energies that permit to use this material as a potential absorber substitute of silicon.

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