ABSTRACT: A comprehensive study on the electronic structure and optical properties of a Cu$_3$N film is performed by the first-principles study using density functional theory. The Hubbard ($U$) term is added in the local density approximation approach for improvement of the theoretical band gap energy. The band structure of the Cu$_3$N unit cell shows a strong hybridization of Cu 3d and N 2p orbitals in the near-valence band region ($M$) because of their antibonding states which are also observed by molecular orbitals (HOMO−LUMO). The conduction band is dominated by a very small amount of Cu 3p and N 2p orbitals. The density of states exhibits a negligible deformation in Cu−N bonding. The Cu$_3$N thin film deposited by the DC magnetron-sputtering technique shows a polycrystalline structure with a nonstoichiometric Cu$_3$N phase. The experimentally obtained optical band gap and refractive index of the Cu$_3$N film are 1.44 eV and 2.14, respectively, which are comparable with those from the theoretical approximation.

1. INTRODUCTION

The quest for new semiconducting materials is always a driving force in the field of materials science. In modern technology, it plays an important role in integrated circuits and optoelectronic research. In recent years, copper nitride (Cu$_3$N) has gained a lot of interest because of its application as an optical storage device in recorded media, laser writing, and as a battery material because of its unique chemical activity. Pure Cu$_3$N has a cubic anti-ReO$_3$-type structure, where the Cu atom is placed in the center with N$_2$ atoms at its corners. Though the Cu$_3$N crystal is an insulator, it transforms into a semiconductor because of its vacancy doping. Previously, the optical properties of Cu$_3$N are reported by several authors including the effect of N$_2$ gas pressure on the optical band gap of the deposited Cu$_3$N films. The theoretical optical band gap of Cu$_3$N is close to ~0.9 eV, but the experimental value depends on various deposition conditions or parameters such as substrate temperature or doping. Sahoo et al. reported that the indirect and direct band gap varies between 1.17−1.68 and 1.72−2.38 eV because of increasing pressure. Xiao et al. also reported the photoluminescence property of Cu$_3$N, where the band gap lies between 1.23 and 1.91 eV. However, an extensive and useful study on the experimental and computational modeling methods on the band structure and optical properties of the metastable Cu$_3$N film is very much needed. Earlier, a lot of reports are available on the density functional theory (DFT) calculations of Cu$_3$N films including the indirect band gap, which is about 0.5 and 0.23 eV, as determined using the generalized gradient approximation (GGA) and the local-density approximation (LDA), respectively. Zakutayev et al. reported the indirect fundamental band gap of Cu$_3$N as 1.0 eV with the combination of the GGA and the Coulomb interaction term $U_d$ (Cu) = 5 eV and GW quasiparticle energy calculations. The position of the charge state of the defect can be in question of uncertainty by this estimation. It is known that the GGA and LDA underestimate the band gaps because of the heavy d-element of Cu and self-interactions. For improving the band gap, the LDA + $U$ approach can be employed, which can improve the band gaps than those in previous theoretical reports.

In this study, we have used the DFT computational approach for studying the crystal structure of cubic Cu$_3$N. The band structure is explained with an indirect band gap calculation applying the LDA + $U$ approach. Among the corrective approaches used to solve the DFT electronic band gap problem is the DFT + $U$ correction method to mitigate this self-interaction error, which adds a Hartree−Fock-like term to localize the electron states such as 3d or 2p orbitals.
When compared with alternative approaches, DFT + U correction has been demonstrated to be reliable than the other methods, however with a vital advantage of significantly lower computational cost. By effectively correcting the electronic structure of the studied system while using the U correction, further accurate predictions of intermolecular interactions and formation energies could be reached. The optical properties are studied with the help of a photon energy calibration and geometry optimization, making certain the standards of convergence for the electronic structure of the Cu3N unit cell contains six Cu atoms, whose fractional coordinates are (0, 0.5, 0.5); (0.5, 0, 0.5); and (0.5, 0.5, 0). The fractional coordinate of N is (0.5, 0.5, 0.5), which is in the center position of the Cu molecules. Figure 1b shows the first Brillouin zone of the Cu3N crystal, which has high-symmetry points G, M, R, and X joined by lines of pink color. The calculated Cu–N and Cu–Cu bond lengths are 1.99 and 2.82 Å, respectively. LDA with the Ceperley–Adler–Perdew–Zunger functional has been used for evaluating the exchange–correlation function. The wave function is expanded as much as 440 eV of plane-wave cutoff energy. To make certain the standards of convergence for the electronic characteristic calculation and geometry optimization, 8 × 8 × 8 k-points were applied for Cu3N. To describe the electron–ion interaction, Vanderbilt-type ultrasoft pseudopotential has been used. The Broyden–Fletcher–Goldfarb–Shanno relaxation plan is useful for optimizing the structure. The structure cell and atomic relaxations are conducted as long as the recurring forces are beneath 0.02 eV. Geometrical search engine optimization was executed making use of the full vitality at 5 × 10−6 V/atom (at an optimum force of 0.01 eV/Å, a maximum tension of 0.02 GPa) as well as the highest atomic displacement of 5 × 10−4 Å.

2. METHODS

2.1. Computational Details. Computational simulations have been done using a DFT-based plane-wave pseudopotential approach. All the computations are carried out using the Cambridge Serial Total Energy Package (CASTEP) performed with Material Studio 8.0.19,20

The 3D cubic structure of Cu3N belongs to the space group Pm3m (no. 221), which is illustrated in Figure 1a. The lattice parameter of Cu3N is a = b = c = 3.837 Å, α = β = γ = 90°. The cubic structure of the unit cell contains six Cu atoms, whose fractional coordinates are (0, 0.5, 0.5); (0.5, 0, 0.5); and (0.5, 0.5, 0). The fractional coordinate of N is (0.5, 0.5, 0.5), which is in the center position of the Cu molecules. Figure 1b shows the first Brillouin zone of the Cu3N crystal, which has high-symmetry points G, M, R, and X connected by lines of pink color. The calculated Cu–N and Cu–Cu bond lengths are 1.99 and 2.82 Å, respectively. LDA with the Ceperley–Adler–Perdew–Zunger functional has been used for evaluating the exchange–correlation function. The wave function is expanded as much as 440 eV of plane-wave cutoff energy. To make certain the standards of convergence for the electronic characteristic calculation and geometry optimization, 8 × 8 × 8 k-points were applied for Cu3N. To describe the electron–ion interaction, Vanderbilt-type ultrasoft pseudopotential has been used. The Broyden–Fletcher–Goldfarb–Shanno relaxation plan is useful for optimizing the structure. The structure cell and atomic relaxations are conducted as long as the recurring forces are beneath 0.02 eV. Geometrical search engine optimization was executed making use of the full vitality at 5 × 10−6 V/atom (at an optimum force of 0.01 eV/Å, a maximum tension of 0.02 GPa) as well as the highest atomic displacement of 5 × 10−4 Å.

2.2. Thin-Film Deposition and Characterization. Copper nitride films are prepared by the DC magnetron-sputtering process. The 2" sputter target was made of oxygen-free copper with a purity of 99.9%. The films are deposited on quartz glass substrates for optical characterization and XRD measurements. All substrates are washed well and ultrasonically cleaned in acetone. The vacuum chamber is evacuated to a base pressure of less than 10−5 Pa by a turbo molecular pump. The working gas with the enclosed sputter chamber was 99.999% pure N2. The N2 gas flow rate is varied between 3.5 and 4.0 sccm. The chamber pressure during the magnetron operation was maintained at 1 Pa. Typical discharge power during the sputter deposition was 100–130 W (discharge voltage 325 V, plasma current 0.4 A). The deposition took place at room temperature and with electrically floating substrates. The films were deposited for 30 min on a quartz glass substrate. After deposition, the films were taken out of the chamber and employed for further characterization.

2.3. Film Characterization. The crystalline structure of the deposited Cu3N thin film is examined by XRD with Cu Kα radiation. The measurements were carried out using a Bruker D8 ADVANCE X-ray diffractometer with a step size of 0.05°. Optical transmission studies were carried out to estimate the band gap of the Cu3N film using a UV–vis double-beam spectrophotometer (PerkinElmer) at a step length of 2 nm in the wavelength range between 300 and 1100 nm. The Cu3N sample is placed in front of the sample beam and the identical glass substrate was placed in front of the reference beam. The ellipsometric measurements have been performed through a spectroscopic ellipsometer S2000 (Rudolph Research) for calculating the optical constants with data analysis software WVASE (Woollam).

3. RESULTS AND DISCUSSION

3.1. First-Principles Calculations. 3.1.1. Electronic Properties. The band structure of the Cu3N unit cell is illustrated in Figure 2a to analyze the electronic properties of Cu3N plotted along the high-symmetry direction of k-points, X, R, M, G, and
Figure 2. (a) Band structure of the Cu₃N unit cell, (b) DOS of the Cu₃N unit cell and the molecular orbitals (c) LUMO and (d) HOMO of Cu₃N.

Figure 3. Electron density of the Cu₃N structure: (a) 2D view and (b) 3D view.

3.1.2. Optical Properties. Optical spectroscopy is the most useful and prominent characterization in modern technology to understand the energy band structure and dielectric properties of solid materials. The photon energy with different frequencies is employed on Cu₃N to obtain the transmittance plot, refractive index, dielectric function, and electrical conductivity. All these simulation plots are determined using the formalism developed by CASTEP.²⁶,²⁷

Figure 4a shows the transmittance plot of cubic Cu₃N as a function of photon energy E. The peak value is observed at an energy of 1.2 eV and the transmission has become almost saturated after a photon energy of 2.8 eV. The optical transmittance of Cu₃N majorly depends on the N₂ flow rate and substrate temperature.²⁸ The Cu content has also influenced the transmittance as it acts as a light-scattering center.³⁰ Cu₃N films are transparent in the IR region and also show interband transitions in the visible region.²⁸ The transmittance of Cu₃N at such an energy level is very much favorable to be used as an optical recording media.³⁰ Figure 4b shows the refractive index of the Cu₃N structure with real and imaginary parts. The maximum value of the real part (concerned with scattering) and the imaginary part (concerned with absorption) is bound at photon energies of 0.5 and 1.0 eV, respectively. The peak value of the real and imaginary part attains values of 2.25 and 1.52, respectively, after which it decreases to become almost saturated at photon energies of 2.0 and 3.0 eV, respectively. The obtained refractive index value is very much comparable to those published by Reddy et al. and Odeh.²⁹–³¹ In the design of optical reflectors, such semi-
conductor optoelectronic devices require a refractive index typically between 2.25 and 2.5 for ambient light propagation.22

The dielectric function explains the response of the semiconductors based on their band structure to the electromagnetic radiation by the interactions of photons and electrons.23 The dielectric function can be determined using the frequency-dependent functions, \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \), which are closely connected to the band structure of a material. The imaginary part of dielectric function \( \varepsilon_2(\omega) \) is acquired in the momentum matrix elements between the occupied and unoccupied electronic states using the following equation20

\[
\varepsilon_2(\omega) = \frac{2e^2}{\Omega_{\varepsilon_2}} \sum_{k,\nu,\sigma} |\psi_k^{\nu}|^2 |\psi_k^{\nu}|^2 \delta(E_k^{\nu} - E_k^{\sigma} - E)
\]

where \( e \) is the electronic charge, \( \omega \) is a vector which defines the polarization of the incident electric field, \( \omega \) is the light frequency, and \( \psi_k^{\nu} \) and \( \psi_k^{\sigma} \) are the conduction and valence band functions, respectively. The real dielectric function can be obtained from the Kramers–Kronig transformation equation

\[
\varepsilon_1(\omega) = 1 + \frac{2p}{\pi} \int_0^{\infty} \frac{\omega'\varepsilon_2(\omega')}{\omega^2 - \omega'^2} d\omega'
\]

where \( p \) signifies the principal value of the integral.

The dielectric functions of Cu₃N are illustrated in Figure 4c. The static dielectric constant can be obtained from the real part at zero photon energy. It is observed that the static dielectric constant of Cu₃N is about 15. The imaginary part decreases exponentially with increasing photon energy, and it becomes almost saturated after a photon energy of 2.8 eV. The real part reveals the band energy at which the photon energy begins and which occurs at a minimum direct band gap.23 Direct transitions are considered in this study; the nonzero value of the imaginary dielectric constant is found between 0 and 1.8 eV because the DFT calculations provide only theoretical approximations to the original material. Kim et al. have explained similar dielectric functions of Cu₃N where the direct d–p interband transitions took place. In the Brillouin zone, the d-like valence band and the p-like conduction band have dispersed in each other parallelly.8

Figure 4d shows the photon energy-dependent electrical conductivity of the Cu₃N structure. The real part has exponentially increased to \( 3.6 \times 10^4 \) S/m and gets saturated. The imaginary part increases to \( 1.5 \times 10^4 \) S/m and gets saturated from 1.9 eV. These values nearly satisfy the previous reports by Du et al.34 The increase in photon energy leads to the formation of excitons which dissociate into free charges. The dependence of the Cu content readily influences the electrical conductance behavior reflecting the percolation mechanism.34 In the Cu₃N structure, Cu resides in the center and acts as an electron donor and thereby increases the electrical conductivity.35 The semiconducting nature of Cu₃N is observed in many reports, where conductivity is explained with an indirect transition from the \( R \) point in the valence band to the \( M \) point in the conduction band.36,37

The XRD patterns (discussed later) of the deposited Cu₃N films have revealed the polycrystalline nature, which satisfies the increasing conductivity of the films.

3.2. Experimental Results. 3.2.1. XRD Analysis. Figure 5 shows the XRD patterns of the deposited Cu₃N thin film with indexed peaks. The polycrystalline single phase of Cu₃N is observed from the diffraction peaks at \( \theta = 23.20^\circ \) (100), \( \theta = 40.64^\circ \) (111), and \( \theta = 47.46^\circ \) (200).35 There is no evidence of pure Cu, as observed in the XRD patterns. The Cu₃N(100) plane has the highest intensity owing to the distinct synthesis process adopted here and follows the principle of preferential growth because of the lowest crystal-free energy.9 A detailed study on the XRD patterns of Cu₃N films is reported in our previous study, where a comparison with the experimental data is shown with simulated patterns.23 The microstructure of the Cu₃N thin film is studied based on its lattice constant (using eq 3), which is calculated from interplanar spacings using Bragg’s law (eq 3)

\[
d_{\text{AB}} = \frac{\lambda}{2 \sin \theta}
\]

Here, \( d_{\text{AB}} \) is the interplanar spacing of particular Miller indices, \( n = 1 \) (order of diffraction), \( \lambda \) is the wavelength of X-rays, and \( \theta \) is the diffraction angle.

The average lattice constant \( a \) of the Cu₃N thin film acquired is 0.3812 nm. The value of the lattice constant is very much close to those of previous reports on the deposition of Cu₃N film by the magnetron-sputtering technique9 and to the simulated results obtained in this research. There is no preferred orientation in the XRD pattern as the non-stoichiometric Cu₃N film has resulted in a lattice constant in the range between 0.375 and 0.384 nm.10 Pierson has explained the effect of the \( N_2 \) flow rate on the stoichiometric phase of the Cu₃N film, which is in good agreement with our result.39 The formation of a Cu₃N phase takes place because of Cu–N bonding as a result of the absorbing \( N_2 \) atom being placed in the Cu lattice. Both the atoms of Cu (having a high kinetic energy) and \( N_2 \) (having a comparatively lower kinetic energy) contribute to the formation of the Cu₃N crystal structure.3

3.2.2. Optical Band Gap Analysis. Figure 6a shows the UV–vis absorption spectrum of the Cu₃N thin film with its corresponding Tauc plot (Figure 6b) to measure the optical band gap. The photon absorption in the Tauc plot is defined by the Tauc relation in eq 5

\[
\alpha \nu = B(\nu - E_g)^{1/2}
\]

In this equation, \( \alpha \) is the absorption coefficient, \( h \) is the Planck constant, \( \nu \) is the photon frequency, \( E_g \) is the band gap energy,
The optical energy band gap ($E_g$) is determined using the curve of $(a h \nu)^{1/2}$ versus photon energy $h \nu$ by extrapolating the line to the abscissa of $h \nu$ according to the standard plot technique of Tauc et al. The indirect allowed transitions of the Cu$_3$N semiconductor are reported by Dorranian et al. The measured optical band gap ($E_g$) at room temperature is 1.44 eV, which is very close to those in previous reports. The optical properties show that the visible light is absorbed maximum in between 500 and 800 nm (Figures 6 and 7), but after 800 nm, it shows a transmission property.

The theoretically simulated value of the band gap energy is about 1.4 eV, which is comparable with the experimentally obtained optical band gap energy (1.44 eV) by UV–vis absorption spectroscopy (Figure 6). The measured band gap here with a lattice constant greater than 0.38 nm (as discussed in XRD Analysis) is very true with the indirect semiconductor Cu$_3$N phase. The dependence of optical band gap varies from the energy level defect, electron transition of Cu atoms, to electron transition at Cu$_3$N grain boundaries. The semiconducting nature of the Cu$_3$N film is related to the electron-density distribution, which is influenced due to the presence of weak localization electrons in the Cu$_3$N lattice with covalent bonding. It also depends on the mobility of Cu and N atoms contributing to Cu$_3$N film growth. The kinetic energy of Cu is more than that of N, while reaching the substrate material; N$_2$ often reacts with Cu and then reaches the substrate. Consequently, the Cu content is very much responsible in determining the growth and conductivity of the Cu$_3$N films.

It is known that the GGA and LDA underestimate band gaps because of the heavy d-element of Cu and self-interactions. For improving the band gap, the LDA + $U$ approach has been employed, and we obtained an improved band gap than the previous theoretical reports. There is a qualitative difference in the LDA and LDA + $U$ approach to give an approximation on the ground-state energy. The perturbative LDA + $U$ calculation is the Hubbard ($U$) potential correction, which has a self-consistent unperturbed value. The strong Coulomb interaction of localized electrons can be treated by an additional Hubbard-like term in the LDA approach, which is not correctly described by LDA and GGA. The Coulomb interactions are especially strong for d and f electrons, but it can be important for p-localized electrons too. However, a huge variety of exchange–correlation functionals are involved in molecular cases that need a sophisticated calculation.

The trace of N 2s electron states is found to have a −15 eV HOMO−LUMO gap, whereas it is −8 eV in the case of N 2p electrons (Figure 2). A small HOMO−LUMO energy gap is essential for low chemical stability because adding electrons to some high-lying LUMO and/or elimination of electrons from the low-lying HOMO are energetically favorable in almost any potential reaction. The low HOMO−LUMO gap in this material predicts highly stable thin films. N 2s shows low chemical stability in the formation of Cu$_3$N. The presence of 2s and 2p electrons with a high HOMO−LUMO gap creates interstitial defects, and because of these defects, the thin film exhibits the polycrystalline property. XRD results also show the polycrystalline single phase of Cu$_3$N film. The metal component Cu 3d shows a very low-intensity valence band (−1 eV). Cu 3d

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**Figure 6.** UV–vis spectrum of the Cu$_3$N thin film: (a) absorption spectrum and (b) the corresponding Tauc plot (inset).

**Figure 7.** Refractive index and extinction coefficient ($k$) as a function of wavelength ($\lambda$) of the deposited Cu$_3$N films. Ellipsometric measurements are performed on a spectroscopic ellipsometer S2000 (Rudolph Research). Data analysis was made with software WVASE (Woollam).

The optical constants are derived by the ellipsometric measurements from a fit using the Cauchy dispersion relation (polynomial). In this process, the real part of the refractive index is about 1.48 in the UV region (300–400 nm), which gradually increased with a peak value of 2.15 at 730 nm and saturated up to 800 nm with the same value, and at 900 nm, it became 2.10. The extinction coefficient ($k$, imaginary part) is 1.85 around 350 nm, which gradually increased up to 530 nm and attained a maximum value of 2.02. Thereafter, it starts to decrease (with small saturation up to 570 nm) gradually up to 900 nm. The peak value of the real and imaginary parts attains values of 2.15 and 2.02, respectively, whereas in theoretical approximation, these values are 2.25 and 1.52, respectively. Both the values of $n$ and $k$ are comparable with those of simulation studies as a function of photon energy (already discussed) and also with those of the previous report. The optical properties show that the visible light is absorbed maximum in between 500 and 800 nm (Figures 6 and 7), but after 800 nm, it shows a transmission property.

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orbital electrons have a major contribution to the DOS simulation spectrum and are the dominating factor in deciding the band gap energy.

4. CONCLUSIONS

The Cu3N film has been deposited by the DC magnetron-sputtering technique. The lattice parameter of the simulated film (0.3837 nm) is comparable with that obtained from the deposited film (0.3812 nm) by the XRD method. The deposited films are polycrystalline with a single Cu3N phase. Strong hybridization of Cu 3d and N 2p orbitals in the near-valence band region (M) takes place because of their antibonding states. The DOS evidenced a negligible deformation of Cu–N bonding. The calculated indirect band gap of the Cu3N film from the first-principles approach with an additional Hubbard term (LDA + U) is 1.4 eV, which is close to the obtained value of 1.44 eV from the UV–vis absorption spectrum. The real part of the refractive index attains a peak value of 2.15, which is in well agreement with the theoretically estimated value of 2.25. The imaginary part of the refractive index shows a difference in the peak value of 0.5 with respect to theory and experiment.

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Notes
The authors declare no competing financial interest.

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