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Strain-Induced Valence Band Splitting Enabling Above-Bandgap Exciton Luminescence in Epitaxial Mg₃N₂ Thin Films

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Nidhi Shukla, Sourav Rudra, Renuka Karanje, Debmalya Mukhopadhyay, Prasanna Das, Bidesh Biswas, Madhusmita Baral, Mukul Gupta, and Bivas Saha*



direct bandgap at room temperature. Growth-induced biaxial tensile strain splits the light hole and split-off hole bands in Mg_3N_2 by ~170 meV, which causes the above-bandgap luminescence. Optical absorption, synchrotron radiation ultraviolet photoemission spectroscopy, and photoluminescence measurements also confirm that Mg₃N₂ is a direct bandgap semiconductor with an exciton binding energy of ~40 meV. First-principles calculations with Heyd-Scuseria-Ernzerhof hybrid-functional support the straininduced valence band splitting and above-bandgap excitonic feature. Room-temperature multiple exciton luminescence in Mg_3N_2 would be useful for visible-light-emitting diodes (LEDs), semiconductor lasers, and other optoelectronic applications.

1. INTRODUCTION

Wide-bandgap (WBG) semiconductors have garnered significant interest owing to their diverse functionalities and widespread technological applications in high-power electronics,¹ light-emitting diodes,²⁻⁴ solid-state semiconducting lasers,⁵ transducers,^{6,7} and as host materials for single-photon emitters.8 A critical characteristic of WBG semiconducting materials is their exciton binding energy (BE) (E_b), which plays a pivotal role in determining their luminescence efficiency.^{9,10} Gallium nitride (GaN), a ubiquitous and industrially vital LED material, exhibits a modest E_h of only 26 meV, limiting its luminescence efficiency.^{11,12} Similarly, while other III-nitride semiconductors like AlN, InN, and their alloys, alongside rare-earth active luminescent materials, have been explored extensively in various optoelectronic devices,^{13–15} they often fall short in terms of luminescence efficiency.¹⁶ In the oxide class of materials, ZnO has a nearly comparable bandgap (\sim 3.37 eV) as GaN (\sim 3.4 eV), but a higher E_b of ~60 meV¹⁰ presents itself as an alternative WBG semiconductor with enhanced luminescence efficiency. Nevertheless, the challenge persists in achieving high-quality p-type

Here, we show conclusive experimental evidence of strain-induced

valence band splitting in epitaxial and stoichiometric Mg₃N₂ thin films that leads to excitonic luminescence above and below its

> ZnO¹⁷ thereby limiting its applications and driving the search for superior alternative materials.

> Mg₃N₂, an II-nitride semiconductor, has attracted substantial interest and exhibits many of the necessary criteria for optoelectronic device applications.¹⁸⁻²¹ The relative abundance of Mg and N combined with a large variety of synthesis methods offers a low-cost production of nontoxic Mg₃N₂ as an alternative candidate for manufacturing economically viable devices. In ambient conditions, Mg₃N₂ crystallizes in an antibixbyite structure (see Figure S1) with a lattice parameter of 9.96 Å.²¹⁻²³ Mg₃N₂ has been long known in the industry as a nitriding agent for the formation of various nitrides such as MgSiN₂ and AlN, as a catalyst for the synthesis of superhard cubic boron nitride, silicon nitride, and used for gas sorption

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Figure 1. (a) HRXRD pattern of Mg_3N_2 thin film deposited on (001) MgO substrate showing the primary diffraction intensity appearing from the (222) planes. A small diffraction spot from the AlN capping layer is also visible. (b) ϕ -scan of asymmetric (440) planes of Mg_3N_2 along with (220) planes of the MgO substrate. 12-equally spaced peaks highlight four twisted 3-fold symmetric triangular domain growth. (c) Fitted XRR pattern of the Mg_3N_2 film shows a thickness of 60 nm. The inset shows the scattering length depth (SLD) profile along the depth of the film. (d) Raman spectra of the single-crystalline Mg_3N_2 thin film with the inset highlighting the main Raman peak from the Mg–N symmetric stretching vibrational mode.

and separation.^{19,24} Experimental research reveals that ceramic Mg_3N_2 has a high thermal conductivity and is a reversible hydrogen storage material.^{25,26} Previous studies on powder and microporous Mg_3N_2 exhibit room-temperature excitonic photoluminescence (PL) in the blue-violet region and intense yellow-orange to red emission from sub-bandgap localized nitrogen vacancy and other complex defect states.^{18,19}

Despite exhibiting such vital properties and applications, a profound investigation into the properties and stoichiometric formation of Mg₃N₂ is still lacking due to its insufficient purity and less reliable synthesis/growth methods. The main issue is inherently associated with its instability, which limits the full utilization of Mg₃N₂ for its direct applicability in optoelectronic devices.^{27,28} Liquid-ammonia synthesis-based microporous Mg₃N₂ exhibits stronger red luminescence associated with multiple defects or impurities than free exciton luminescence.¹⁹ However, until now, little attention has been paid to improving excitonic luminescence by reducing the defect-limited broad-band yellow-orange or red luminescence. Therefore, probing detailed spectroscopic and electronic structural studies in epitaxial stoichiometric Mg₃N₂ thin films is highly desired. Moreover, applying external perturbation, such as the effect of strain on Mg₃N₂'s electronic structure, could lead to novel emission properties that would be useful for many device applications. Here, we present a detailed microscopic analysis of the structural, electronic, optical, and excitonic PL in epitaxial Mg₃N₂ thin film and also show straininduced valence band splitting that leads to above-bandgap exciton PL.

2. RESULTS AND DISCUSSION

2.1. Structural Characterization. The as-deposited Mg_3N_2 thin film, capped with a 10 nm layer of AlN, exhibits a greenish-yellow hue. To ensure structural and optical characterization accuracy, the thickness of the AlN capping layer is limited to 10 nm, effectively shielding the sample from oxidation under ambient conditions and enhancing its stability without compromising its properties. The symmetric $2\theta - \omega$ high-resolution X-ray diffraction (HRXRD) pattern of Mg₃N₂ deposited on (001) MgO substrate (see Figure 1a) reveals distinct reflections from (222) and (444) planes. The full width at half-maxima (FWHM) of the ω -scan (rocking curve) corresponding to the (222) plane measures 2.9° (see Figure S5a), indicating tilted growth of Mg_3N_2 planes, suggestive of sample texturing or mosaicity. Previous studies²⁹ attribute similar broadness to lattice rotation induced by threading dislocations, stacking faults, and misfit dislocations at the filmsubstrate interface, resulting in misorientations and a two-layer film structure. Additionally, the HRXRD pattern (depicted in Figure S6 in the Supporting Information) confirms the stability of Mg₃N₂ after four months of storage in a vacuum chamber, despite prolonged exposure to atmospheric conditions during various measurements.

The epitaxial growth of the film is further corroborated by the ϕ -scan of asymmetric reflections, such as (440) and (004). The results of the ϕ -scan reveal a 12-fold symmetry (see Figures 1b and S4), indicative of four twisted 3-fold symmetric triangular domain growth.²⁵ The rocking curve of the (440) reflection demonstrates a FWHM of approximately 1.65°



Figure 2. XPS core level spectra of Mg_3N_2 thin film with AlN capping layer exhibiting (a) Mg 2p and (b) N 1s orbital peaks as a function of BE. (c) N *K*-edge XANES spectra of Mg_3N_2 thin film deposited on (001) MgO substrate with a capping layer of ~5 nm W compared with the theoretically calculated one.

(shown in Figure S3b). Additionally, we have identified an inplane tensile strain of around 1.2% and an out-of-plane compressive strain of about 0.8% in the film using the measured out-of-plane and in-plane lattice parameters from the $2\theta - \omega$ scan of symmetric (222) and asymmetric (004) planes (Section 2 and Figure S2 in the Supporting Information). It is noteworthy that a slight asymmetry in the (004) reflection is discernible from the XRD pattern, indicating the presence of the in-plane strain. Prior microstructural studies have also reported similar tensile strain in thicker films exceeding 20 nm due to grain coalescence, a phenomenon observed in other epitaxial films as well.²⁹⁻³² In the current scenario, the film thickness measures 60 nm, as determined by X-ray reflectivity (XRR) measurements, satisfying the criteria for tensile strain in the film. The XRR fitting also provides an AlN capping layer thickness of 10 nm and surface roughness of approximately 1 nm. The obtained mass density of Mg₃N₂ from XRR analysis is 2.7 g/cm^3 , in good agreement with the theoretical value of 2.74g/cm^{3,33} suggesting the suppression of vacancy density (most likely nitrogen vacancy) in the current film. A SLD profile, visible in the inset of Figure 1c, indicates the formation of a thin interfacial layer of lower density between the film and substrate.

Moreover, the Raman spectrum of Mg_3N_2 (see Figure 1d) reveals a prominent peak accompanied by faint features at 380 and 660 cm⁻¹, respectively. The intense peak at 380 cm⁻¹ stems from the strong Mg-N symmetric stretching vibrational mode.^{21,28,34} The weak peak at 660 cm⁻¹ corresponds to the higher energy longitudinal optical (LO) phonon vibration in Mg_3N_2 . Our density functional theory (DFT) calculation suggests that the highest LO phonon energy at Γ is 79.1 meV close to the experimentally observed Raman peak at 660 cm⁻¹. Symmetry analysis of the phonon modes further confirms the experimentally observed Raman active modes to be of T_{σ} symmetry at the Γ -point. The complete phonon dispersion, including nonanalytic corrections at Γ , is illustrated in the Supporting Information Section 4. It is worth noting that the potential decomposition product of Mg₃N₂ would manifest as an additional Raman mode at 441 and 1080 cm^{-1,18,28} The absence of such Raman modes in our measurement signifies the film's protection from decomposition.

2.2. Electronic Structure Analysis. The core-level electronic structure and chemical shift are determined from

X-ray photoemission spectroscopy (XPS) measurements by observing the Mg 2p and N 1s peaks, as shown in Figure 2a,b. The Mg 2p peak exhibits a little asymmetry toward the higher BE side, which is deconvoluted with two subpeaks, one at 50.22 eV and the other at 51.25 eV. The major peak at 50.22 eV is due to the Mg-N bond,³⁵ and the minor shoulder peak at 51.25 eV represents the formation of Mg $-O_x-N_y$. This type of oxynitride peak at a higher BE side is present in other nitride systems also. $^{36-38}$ However, due to the lower atomic number (Z = 12), the spin-orbit coupling (SOC) is extremely weak in Mg. As a result, the separation between the Mg $2p_{3/2}$ and $2p_{1/2}$ peaks is very small to resolve if the FWHM of individual peaks is larger than their separation. Previous literature from Aballe et al. mentioned that the SOC energy in bulk Mg is 0.27 eV,³⁹ which is much smaller than the FWHM of the main Mg 2p XPS peak (FWHM ~1.34 eV), as shown in the manuscript. Due to this limitation and room-temperature experimental peak broadening, resolving the SOC components in the XPS peak fitting for Mg 2p is very difficult. The N 1s peak was deconvoluted into three different subpeaks located at 396.3, 396.9, and 400.62 eV, respectively. The lowest energy subpeak at 396.3 eV is assigned to the nitrogen bonded with metallic Mg in stoichiometric Mg₃N₂ as compared with the N 1s of other transition metal nitrides such as CrN and HfN.^{40,41} The quantitative analysis of the area under Mg 2p and N 1s XPS peaks shows the stoichiometric ratio of Mg/N 1.56, which is close to the ideal stoichiometry of 1.5 for defect-free pure Mg₃N₂. The slight deviation from the ideal stoichiometry is due to the presence of slight native impurities, such as oxygen and carbon, in our film, as indicated by the XPS survey scan. The middle peak at 396.9 eV corresponds to the C-N bonding, and the higher BE peak at 400.7 eV represents the small amount of N–O (interstitial nitrogen atom making bond with native oxygen) bonding present in the system comparable with the similar peaks present in carbon nitride film synthesized under N₂/CH₄ dielectric barrier discharge plasma.⁴² The source of native oxygen and carbon in Mg₃N₂ can be from either the contamination of targets or the background chamber during the growth. The full-range XPS survey scan of Mg₃N₂ comparing XPS spectra of different sputtering times is presented in Supporting Information Section 6.

To further investigate the electronic structure and bonding states, XANES measurements are performed at the N K-edge in the Mg₃N₂ thin film with a \sim 5 nm tungsten (W) capping layer. It is important to mention that while an AlN capping layer is used in this study for all the measurements, a W capping layer is used for the XANES measurements to prevent any interference from the nitrogen signal from AlN. The normalized N K-edge XANES spectra of the Mg₃N₂ film, along with the theoretically calculated spectra (adapted from the FEFF modeling results of Materials Project),³³ are presented in Figure 2c. The XANES spectral features designated as A, B, C, and D match almost well with the theoretically calculated ones, confirming the formation of Mg₃N₂. Such features in the N Kedge spectrum are associated with the transition from the core N 1s level to antibonding N 2 ps – Mg 3 ps hybridized states. Theoretically calculated density of states (DOS) shows that the valence band edge near the Fermi-level is mostly dominated by N 2p states, similar to other nitrides, 37,43,44 and conduction band states appear from the hybridization of N 2p, 2s and Mg 3s, 3p orbitals.^{22,23} The peak A (~404.9 eV) at the edge onset is assigned to the N 1s π^* transition, and the prominent B peak (~410.9 eV) corresponds to the N 1s σ^* transition.⁴⁵ Such antibonding states originate through N 2ps - Mg 3ps hybridized states. The higher energy spectral features C, D, and above (not marked) may be attributed to higher-lying hybridized states of N and Mg orbitals. The relatively suppressed intensity of the pre-edge A-peak can be understood due to higher absorption of the W capping layer and the associated interface, resulting in a weak signal from the underneath Mg_3N_2 layer as the total electron yield (TEY) mode is sensitive only to the near-surface region.

Furthermore, for a detailed understanding of the valence band DOS in Mg₃N₂, synchrotron radiation ultraviolet photoemission (SR-UPS) spectra were obtained and analyzed with first-principles electronic structure calculation (see Figure 3a,b) for the first time. The top AlN capping layer was etched out completely by sputtering with a 1 keV Ar^+ beam for 50–65 min with a very small AlN signal in the survey scan data, as shown in Supporting Information Section 6. The valence band is found to be broad, with a dominant contribution from Mg₃N₂ along with native defect states. The experimental UPS data suggest that the valence band edge is positioned at ~ 1.87 eV from the Fermi level, which is lower than the bandgap value. The Fermi level for the pristine and relaxed Mg₃N₂ is 30 meV above the valence band maxima from the DFT calculation, which is quite small compared to the experimental value. This mismatch appears due to the presence of native oxygen defects observed in the XPS survey scan, which turns the system intrinsically *n*-type with a Fermi level close to the conduction band. Some valence band smearing known as Urbach tailing is also observed in the UPS data, suggesting the possibility of the presence of *p*-type impurities in the film. The *p*-type defects might be coming from carbon impurities present in the film as confirmed by the C 1s peak in the XPS survey scan, although the peak is substantially quenched with larger sputtering times (see Supporting Information Figure S12). The possible sources of C could be the target impurities or the background pressure in the sputtering chamber. Although it is very difficult to find the exact origin of C in as-deposited films, the presence of C contamination and metal-carbide formation during the growth of transition-metal nitrides using magnetron sputtering has been reported previously in some literature.⁴⁶



Figure 3. (a) SR-UPS spectra of Mg_3N_2 thin film after etching out 15 nm AlN capping layer. (b) Valence band electronic structure (the total and projected DOS) shows N 2p and Mg 3s hybridized states along with the contributions from native defect states such as C 2p, 2s and O 2p, 2s. Inside the valence band, a strong contribution comes from the N 2s state from Mg_3N_2 . The valence band edge of DFT calculated DOS aligns with the experimental valence band edge from SR-UPS spectra, as shown by a black dotted line. The Fermi level is set at zero.

To model the UPS data, we calculated the DOS of both pristine and native oxygen- and carbon-doped relaxed Mg₃N₂ from DFT calculations under the generalized-gradient approximation (GGA) scheme. Although strain is present in the film, we have checked that the effect of strain on the overall DOS and peak positions is very small, as shown in Figure S14d. Due to the amphoteric nature of carbon as a doping element in nitrides, 47,48 we have explored in theory both the possibility of C in the N site (C_N) as well as the Mg site (C_{Mg}) . The valence band edges for different cases are aligned with the experimental one for further comparison. The threshold peak in UPS with the BE of \sim 3.4 eV is attributed to the N 2p states of Mg₃N₂ from DOS calculations. The major peak with a BE of \sim 6.2 eV is dominated by hybridized Mg 3s and N 2p states along with the contribution of O 2p with a calculated BE of ~6.23 eV. However, the experimental UPS peak appears as one peak with broadening toward the higher BE side due to instrumental and temperature broadening and the presence of a small amount of oxygen and carbon as native impurities. C 2p contributes to this broadening only for the $O_N + C_{Mg}$ defect configuration. The observed peak at \sim 10.9 eV is assigned with the C 2s peak in the DOS at BEs of ~9.7 eV and ~10.4 eV for $C_{\rm N}$ and $C_{\rm Mg}$ defect configurations, respectively. We have also observed a Č 2p peak ~0.4 eV above the valence band edge for the C_N case, consistent with the previous literature report.48,49 The C 2p states overlap with the N 2p causing the Urbach tailing of the valence band edge.

The second observed peak at the BE of ~15.6 eV appears from strong N 2s states of Mg_3N_2 with the calculated BE ~ 14.0 eV, slightly lower than the experimental one. We have assigned all of the observed peaks in the UPS survey scan (see Figure 3a). The higher intensity peak corresponds to the Mg 2p state, showing a large photoemission cross section. A comparison of UPS spectra with different sputtering times is shown in Supporting Information Figure S13. Although we have assigned contributions from orbitals of several elements



Figure 4. (a) Optical transmission and reflection spectra of the Mg₃N₂ thin film deposited on a double-sided polished (001) MgO substrate. The inset represents the region near the band edge transition. (b) Tauc plot of Mg₃N₂ thin film corresponds to a direct bandgap of ~2.89 eV. (c) Real (ε_1) and imaginary (ε_2) parts of the dielectric permittivity of a Mg₃N₂ thin film from ellipsometry data fitting.



Figure 5. PL emission spectra of Mg_3N_2 thin film obtained at (a) 300 and (b) 60 K. Deconvolution of the PL spectra using Gaussian subpeaks represents both direct band-to-band free excitonic and defect-mediated luminescence. (c) Schematic band diagram shows the corresponding optical transitions.

to the VB, the DFT calculated PDOS of such orbitals appears quite sharp and does not consider the aforementioned broadening issue and unknown photoionization cross section of those orbitals at the used excitation energy (~200.9 eV). The presented XPS, XANES, and UPS measurements reveal the formation of the Mg₃N₂ phase and clarify that the film is protected against moisture with the proper choice of the capping layer.

2.2.1. Optical Properties. After confirming the epitaxial growth and phase formation of the Mg_3N_2 film, detailed optical measurements were performed to estimate the optical bandgap, nature of electronic transition, and dielectric permittivity. The optical transmission and reflection spectra (see Figure 4a) show that the film becomes transparent in the visible wavelength above ~450 nm. An abrupt drop in transmission and reflection spectra at a wavelength below ~450 nm corresponds to the main bandgap absorption of Mg_3N_2 . Besides, some more features (marked by an asterisk in Figure 4a) are also apparent above the bandgap energy with a dip in the reflection exhibiting the presence of some other interband transitions. Furthermore, an important feature appears near the band edge transition, as shown in the inset

of Figure 4a. This unambiguous peak profile near the fundamental absorption band edge can be attributed to the inclusion of excitonic effects due to the increased excitonic DOS near the band edge. To further elucidate this, PL measurement has been carried out and discussed below.

A direct optical bandgap as determined from the Tauc plot is 2.89 eV at room temperature (see Figure 4b), consistent with the previous report on thin film and microporous Mg₃N₂.^{19,25} The DFT calculation also reveals the bandgap nature to be direct,²² as confirmed by the optical studies. The obtained dielectric spectra of Mg₃N₂ from ellipsometry data fitting are presented in Figure 4c, which shows the semiconducting nature of Mg₃N₂ matches well with previous theoretical calculations with random phase approximation.⁵⁰ The experimental data are fitted with one Tauc-Lorentz (oscillator strength of 3.21) and two Gaussian oscillator models (oscillator strengths of 3.14 and 1.47), which are suitable for semiconductors. The real part of the dielectric constant (ε_1) of Mg_3N_2 is strictly positive in the entire 210–2500 nm spectral range, which signifies its dielectric nature. Moreover, the optical loss or imaginary component of the dielectric permittivity (ε_2) in the near-infrared spectral range is very

low, highlighting the absence of Drude absorption. The peak in the imaginary part of dielectric permittivity (ε_2) at ~446 nm is attributed to the direct bandgap absorption. The higher energy peak at ~254 nm corresponds to the interband transition from higher-lying conduction states. The dielectric constant (ε) and refractive index (n) in the long wavelength limit are 4.58 and 2.14, respectively, in good agreement with the previously reported value of n.⁵¹ Furthermore, this is consistent with its direct bandgap of ~2.8 eV and matches well with other nitride semiconductors, such as Al_xSc_{1-X}N, having similar bandgaps.⁵² These results, therefore, strongly prove the semiconducting (dielectric) nature of Mg₃N₂ which is also corroborated by optical absorption, PL, and first-principles results.

2.2.2. Photoluminescence Emission. Previous literature reports on PL spectra of commercial bulk-Mg₃N₂ powder and nanostructured microporous Mg₃N₂ exhibit two emission bands in violet-blue ($\sim 2.8-3.0$ eV) and yellow-orange to red ($\sim 1.6-2.2$ eV) spectral ranges.¹⁸ The red emission in microporous Mg₃N₂ was found to be much more intense and broader than the violet-blue emission under UV excitation (~366 nm).¹⁹ To the best of our knowledge, no literature report is available on the PL study in the thin film Mg₃N₂ exploring the effect of strain. Since the defect plays a detrimental role in quenching the main excitonic emission, the role of such defect can be tailored to enhance the PL luminesce and will also be important to investigate. Theoretical calculations suggest nitrogen vacancy (V_N) in Mg₃N₂ as the source of the yellow-orange sub-bandgap luminescence.⁴⁸ However, in the present study, under optimized growth conditions with tuning the deposition pressure during growth (~8 mTorr), we have succeeded in achieving Mg_3N_2 films with reduced V_N defects. This is validated by the observed PL emission (see Figure 5) with much lower defect-limited vellow-orange to red emission compared with intense violetblue excitonic emission, even at room temperature.

The violet-blue ($\sim 2-3.5$ eV) PL spectrum is deconvoluted into five well-separated distinct features, labeled from 1 to 5 (see Figure 5), and the corresponding peak positions for 300 K are noted in Table 1. We have assigned those peaks using the

Table 1. Deconvoluted PL Spectral Features of Mg_3N_2 Film at 300 K

peak labeling	peak positions (eV) $\lambda_{ex} = 3.6 \text{ eV}$	transition nature
1	2.85 (violet)	light hole valence band direct (FX_A)
2	2.69 (blue)	second-order LO phonon replica
3	3.02 (magenta)	spilt-off hole valence band direct (FX_B)
4	2.57 (cyan)	C _N impurity
5	2.25 (orange)	V _N defects
6	1.73 (red)	V _{Mg} + O _N defects

standard DFT calculations from existing literature and our simulation results. The most prominent peak at ~2.85 eV is marked as '1,' which is assigned to the free excitonic transition near the band edge (FX_A), and the secondary emission as a shoulder peak in the lower energy side (marked as '2') at ~2.69 eV corresponds to the second-order LO phonon replica (FX_A - 2LO). We have assigned the phonon replica corresponding to two LO phonon modes with LO phonon energy ~80 meV. The highest LO phonon energy at Γ is 79.1 meV obtained from the DFT calculation (see Supporting

Information Section 4 for details). The absence of 1LO is due to the centrosymmetric nature of cubic Mg_3N_2 as reported for other centrosymmetric systems such as Cu_2O .⁵³

Besides free exciton luminescence and its LO phonon replica, an unambiguous peak (marked by '3') is also present toward the higher energy side of the near band edge free exciton. This above-bandgap shoulder peak has never been observed in the previous PL studies of commercial powder and microporous Mg_3N_2 . This represents the presence of two different kinds of intrinsic excitons named A and B in the Mg_3N_2 thin film. The B excitonic feature is more prominent at low temperatures (Figure Sb in the main text and Figure S9 in the Supporting Information).

The strain-induced valence band splitting into the light hole (LH) and split-off hole (SH) at the zone center causes the above-bandgap excitonic luminescence as corroborated with the first-principles DFT calculation. The calculated Heyd-Scuseria–Ernzerhof (HSE) electronic band structure of Mg₃N₂ with 2% in-plane tensile strain (see Figure 6a and inset) shows that the Γ -point degeneracy of the LH and SH at the valence band lifts along with a band-ordering reversal (see Supporting Information Section 7 for detailed discussion), opening an energy gap of ~100 meV, slightly underestimates the obtained experimental value. Due to the band-ordering reversal caused by the biaxial tensile strain, the LH band appears to be at the top of the valence band, with the heavy hole (HH) bands lowered (see Figure S15a,b). Further calculation of the transition dipole moment (Figure 6b) reveals a strong transition probability between the LH, HH, SH, and conduction band states near Γ . These types of A and B excitonic features have been reported previously in strong SOC materials such as Cu2O and transition metal dichalcogenides.^{54,55} Previous reports on ZnO microwires and thin film GaAsN alloy show that strain can also lift the valence band degeneracy by observing both above (named as B exciton) and below (named as A exciton) bandgap excitonic luminescence features.^{56,57} However, with varying growth pressure, film thickness, and substrates, the uniformity and amount of strain can be altered, and that in turn impacts the above-bandgap excitonic PL properties of Mg₃N₂ thin films (see Supporting Information Section 5 and Figure S10).

Furthermore, we calculated exciton BE from both the experimental PL data and the Wannier-Mott exciton model in theory. The Wannier-Mott exciton model assumes the bound electron-hole pair as a hydrogenic system with the BE E_b = $\mu R_{\infty}/m_0 \ \epsilon^2$, where μ is the reduced mass in units of free electron mass m_0 , R_∞ is the Rydberg constant, and ε is the static dielectric constant of the medium which hosts the exciton.⁵⁸ Using previously reported⁵⁹ room-temperature effective mass of electrons and holes, the reduced mass μ turns out to be 0.2 m_0 . With this and the obtained experimental long wavelength dielectric constant ε of 4.58, the calculated exciton BE is ~130 meV, indicating the possibility of the room-temperature excitonic features in Mg_3N_2 which is further verified in experimental PL measurement. Calculated experimental BE from the difference of bandgap (E_{σ}) and near band edge emission (E_{ex}) comes out to be ~40 meV for Aexciton, which is higher than GaN at room temperature. However, the determination of exciton BEs for both the peaks labeled as 1 and 3 (A- and B-excitons) by the fitting of the quenching of PL emission intensity with the increase in temperature from the Arrhenius model,^{60,61} considering only one nonradiative recombination channel, comes to be 35.51



Figure 6. (a) First-principles DFT calculated electronic band structure of biaxial 2% tensile-strained Mg_3N_2 shows a significant amount of valence band splitting between LH and SH. The inset shows the zoomed-in region near the Γ -point with proper labeling of the LH, HH, and SH bands. (b) Square of the magnitude of the transition dipole moment (TDM) from several valence band states to the conduction band states shows a strong dipole transition near the zone center (Γ).

and 32.60 meV, respectively (see Supporting Information Section 5 and Figure S11). Such a higher BE stabilizes the exciton in Mg_3N_2 against thermal dissociation at room temperature. Although the calculated exciton BE is slightly higher than the experimental, one reason could be the choice of an approximate model to describe exciton, which opens the possibility of a detailed excitonic study in such materials as a future avenue. The obtained value of E_b for Mg_3N_2 is comparable with other oxide semiconductors such as Cu_2O (~86 meV)⁶² and ZnO (~60 meV).¹² Furthermore, an exact estimation of E_b along with the fine structure of PL and more accurate values of the analogous transition require detailed and dedicated PL investigation, which is not the scope of the current work.

The other sub-bandgap emission such as peak '4' at ~2.57 eV is attributed to the transition from C_N defect states inside the gap according to the previous DFT calculation by Yang et al., incorporating different types of defects in Mg₃N₂.⁴⁸ Although the theoretically calculated emission is at ~2.25 eV, it is slightly lower than the present experimental scenario. The peak '5' at ~2.25 eV is due to the presence of $V_{\rm N}$ in the system, consistent with previous literature reports. 18,48 The much lower intensity of peak 5 indicates the presence of a very small amount of V_N in the system, with significant quenching of yellow-orange emission. The lower sub-bandgap emission peak at ~1.73 eV is ascribed to Mg vacancy (V_{Mg}) and associated defect complexes such as V_{Mg} - O_N , ⁴⁸ similar to the Ga vacancy defect complexes responsible for the yellow luminescence in GaN.⁶³ The defect-mediated PL peaks are relatively broadened than the excitonic ones, indicating the presence of a strong electron-phonon coupling in Mg₃N₂.⁶³ The small shoulder peak with very low intensity in the 60 K PL data at higher energy ~ 3.22 eV (see Figure 5b) is due to the defect-mediated below bandgap PL signal coming from the ~10 nm AlN capping layer.⁶⁴ The signal is not present at 300 K because of the thermal quenching phenomenon. With an increase in temperature, the generation of phonons leads to an increase in the nonradiative recombination and quenches of the PL peak. This has already been explored in great detail in other nitrides as well.^{65,66} The current PL measurement data show a fairly weak yellow-orange to red emission compared to the violet-blue PL counterparts, indicating much reduced defect density in the film. The present findings indeed give vital information regarding the band structure and transitions,

which are strongly influenced by the inclusion of strain in the film.

3. CONCLUSIONS

In conclusion, we present the first conclusive experimental report of both above- and below-bandgap exciton luminescence in epitaxial nominally single-crystalline II-nitride semiconducting Mg₃N₂ thin films. Optical spectroscopic analysis reveals that Mg₃N₂ is a direct bandgap semiconductor of 2.89 eV. The effect of strain in the film is manifested in the valence band splitting of LH and SH bands. Such a splitting in the valence band is found to enable two intrinsic A- and B-type free excitonic transitions. The experimental outcome is validated by the density function theoretical calculation. A faint red emission related to the vacancy of Mg and its defect complexes is also evident, along with room-temperature violetblue-free excitonic luminescence in the Mg₃N₂ thin film. Our results demonstrate strong room-temperature exciton luminescence in the violet-blue spectral range and other inherent optical properties of Mg_3N_2 thin film with less vacancy defects. The outcomes in the present case pave the way to understand the role of strain and defects influencing the band structure and excitonic transitions in Mg₃N₂, with potential applications in visible light emitters like white LEDs as well as other roomtemperature excitonic and optoelectronic devices.

4. EXPERIMENTAL AND COMPUTATIONAL METHODS

4.1. Growth Details. Mg₃N₂ thin films were deposited on single crystalline (001) MgO substrates inside an ultrahigh vacuum chamber with a base pressure of 2×10^{-9} Torr, using a reactive DC-magnetron sputtering system (PVD Products, Inc.). Before the deposition, substrates were cleaned with acetone and methanol for 15 min in the ultrasonic bath. The substrate temperature (T_s) was maintained at 773 K during the deposition. The Mg target of 2 in. diameter and 0.25 in. thickness was pre-sputtered for 30 min before the deposition to clean the target from any surface contamination. The films were deposited by sputtering out the Mg target (99.993% purity) at 50 W, maintaining an Ar/N₂ gas mixture ratio of 9:2 standard cubic centimeters per minute at a deposition pressure of 8 mTorr. To prevent moisture-induced oxidation, a capping layer of AlN with a thickness of ~10 nm was also deposited in situ on top of the film. From XRR analysis, the growth rate of Mg₃N₂ was found to be 0.67 nm/min. Mg₃N₂ films were also deposited on double-sided polished (001) MgO substrates for transmission measurements.

4.2. HRXRD. High-resolution thin film X-ray diffraction (symmetric $2\theta - \omega$ scan, ω scan, and ϕ scan) of Mg₃N₂ films on (001)

MgO substrates was performed using the Rigaku SmartLab X-ray diffractometer with Cu– K_{α} X-ray source. The rotating anode X-ray generator was set at 4.5 kW during the measurement. Parallel beam optics with a multilayer X-ray mirror, a Germanium (220) 2-bounce channel cut monochromator, and a Germanium (220) 2-bounce analyzer were utilized for the measurement. XRR fitting was performed using Parratt32 software.

4.3. Raman Spectroscopy. Raman spectroscopy measurements were performed with Renishaw Raman microscopy in the back-scattering mode with 532 nm excitation and grating lines of 2400 per mm.

4.4. Synchrotron Radiation Photoemission Spectroscopy and XANES Measurements. XPS and ultraviolet photoemission measurements were performed at the BL-10 Indus-2 synchrotron source at Raja Ramanna Centre for Advanced Technology, Indore, India.⁶⁷ The sample surface was sputtered with a 1 keV Ar⁺ beam for 65 min to completely remove a 15 nm AlN capping layer. The XPS measurements were recorded for the incident monochromatic photon energy of 696.8 eV. BE was calibrated with respect to a Au foil.

The valence band spectra were obtained at room temperature using synchrotron radiation-based photoemission spectroscopy (PES) measurement with an incident energy of 200.9 eV by employing a PHOIBOS-150 hemispherical electron analyzer. The vacuum inside the analysis chamber during the measurement was maintained at ~9 $\times 10^{-11}$ mbar.

XANES spectra were recorded in TEY mode at soft XAS beamline BL-01 of the Indus-2 synchrotron source. A Mg₃N₂ film with a capping layer of W ~ 5 nm was used for the XANES measurement to avoid the N signal from AlN. To enhance the visibility of the features, the N K-edge spectrum was renormalized first by normalizing the signal by the incident beam energy profile: $I_{TEY}(E)/I_0(E)$, where $I_{TEY}(E)$ is the N K-edge from the Mg₃N₂ sample and $I_0(E)$ is the incident flux. This normalization method is standard for compensating variations in the incident flux and correcting unwanted absorptions from beamline optics features. Second, the pre- and post-normalization procedures were performed using Athena software, resulting in increased feature visibility. XPS spectra were fitted by using XPSPEAK41 software.

4.5. Optical Characterization. Optical properties of Mg₃N₂ films were measured in the reflection mode at three different incident angles (55, 65, and 75°) using a variable angle spectroscopic ellipsometer (VASE) (J.A. Woollam Co.). The experimental Psi (ψ) and Delta (Δ) spectra were fitted using a Tauc-Lorentz and Gaussian oscillators model in CompleteEASE software to extract the dielectric permittivity, refractive index, and extinction coefficients. The fitting was carried out using the Gaussian and Tauc-Lorentz oscillators model to describe the interband transition in the visible spectrum range. Measurements of both the reflection (R) at an incident angle of 24° and the transmission (T) at an incident angle of 0° were also carried out using the VASE machine. The absorption coefficient (α) of Mg₃N₂ film was calculated from the measured reflection and transmission coefficient using the following equation $\alpha = (2.303/d) \times$ (1 R-T), where d is the film thickness. The bandgap was determined from the Tauc plot using the following equation $(\alpha h\nu)^n = A(h\nu - E_{\alpha})^{68}$ where A is a constant, $h\nu$ is incident photon energy, and E_{g} is the material bandgap. The value of n determines the nature of the electronic transition, either direct or indirect.

4.6. Photoluminescence Measurements. PL spectra were recorded using an Edinburgh Instruments model FLS 1000 using a xenon arc lamp source of excitation wavelength 350 nm and visible PMT detector. A liquid-helium-cooled cryostat was used during the temperature-dependent PL emission measurements from 60 K to room temperature. The PL spectra were fitted by using the Fityk software.

4.7. Computational Details. First-principles DFT as implemented in the VASP (Vienna Ab initio Simulation Package) software⁶⁹ was used to calculate the electronic band structure, DOS, and phonon dispersion in Mg_3N_2 . Both the GGA⁷⁰ and HSE06 hybrid functional⁷¹ calculations were carried out with the projected augmented wave pseudopotentials⁷² for both Mg and N atoms. The

plane-wave basis cutoff energy was set to be 550 eV. The gammacentered Brillouin zone was sampled using $4 \times 4 \times 4$ k-mesh for the HSE calculation and $8 \times 8 \times 8$ k-mesh for GGA calculation with a 40 atom primitive unit cell of Mg₃N₂. The nonlocal Hartree-Fock exchange mixing parameter in the HSE calculation was set to be 0.30 to achieve an accurate agreement with the experimental bandgap. The atomic positions were relaxed using the conjugate gradient algorithm until the forces on individual atoms became less than 0.005 eV/Å. For all of the defect calculations, 80 atom supercells of Mg₃N₂ with 4×4 × 4 k-mesh under the GGA scheme were used to find the valence band DOS. Phonon dispersion of Mg₃N₂ was calculated in a finitedifference approach in the supercell method as implemented in the Phonopy code.⁷³ A 2 \times 2 \times 1 supercell containing a total of 160 atoms for the phonon calculation was used. Raman active phonon mode symmetry at the Γ -point was determined using the "IR Raman and Hyper-Raman Modes" utility of the Bilbao Crystallographic Server.⁷⁴ Transition dipole moment analysis between valence and conduction band states was done using the VASPKIT package.⁷

ASSOCIATED CONTENT

Data Availability Statement

The data that supports the findings of this study are available from the corresponding author upon reasonable request.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.4c00524.

Details of the crystal structure of Mg_3N_2 , HRXRD, phonon dispersion spectrum of Mg_3N_2 , temperaturedependent PL, and other supporting DFT results (PDF)

AUTHOR INFORMATION

Corresponding Author

Bivas Saha – Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; International Centre for Materials Science and School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; o orcid.org/0000-0002-0837-1506; Email: bsaha@jncasr.ac.in, bivas.mat@gmail.com

Authors

- Nidhi Shukla Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India
- Sourav Rudra Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India
- **Renuka Karanje** Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India
- **Debmalya Mukhopadhyay** Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India
- Prasanna Das Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; International Centre for Materials

Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

- Bidesh Biswas Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India; Orcid.org/0000-0002-7516-3299
- Madhusmita Baral Electron Spectroscopy and Materials Laboratory, Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India; Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094, India
- Mukul Gupta UGC-DAE Consortium for Scientific Research, Indore 452017, India; orcid.org/0000-0002-9622-656X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.4c00524

Author Contributions

N.S. and S.R. contributed equally to this work. All authors discussed and contributed to the preparation of the manuscript.

Notes

The authors declare no competing financial interest.

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