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The effect of dielectric confinement on photoluminescence of In₂O₃-SiO₂ nanocomposite thin films incorporated by nitrogen

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Nanocomposite thin films containing In_2O_3 nanoparticles were prepared by the target-attachment sputtering utilizing the InN pellets and allowing the N_2 inlet gas flow during the deposition process. The x-ray photoelectron spectroscopy revealed that the chemical composition of In_2O_3 nanoparticles becomes InO_xN_y and the SiO_xN_y phase forms in the matrix of nanocomposite layer. Photoluminescence analysis indicated that the dielectric confinement effect induced by the N-incorporation tends to restrain the green emission of nanocomposite layers due to the presence of surface polarization on nanoparticles. Suppression of blue emission was also observed due to the elimination of oxygen vacancies in In_2O_3 nanoparticles. Furthermore, the N elements might occupy the oxygen lattice sites and generate a new defect level, N_O^- , to induce the violet emission. Analytical results confirmed the mechanisms of green and blue emissions of the nanocomposite thin films containing In_2O_3 nanoparticles reported previously. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4803877]

I. INTRODUCTION

Semiconductors of nanoscale dimensions have attracted considerable research interest owing to their unique physical properties, particularly, their luminescence properties for applications in advanced optoelectronics. 1,2 For instance, the characterizations of semiconductors in quantum dot (QD) or nanoparticle form embedded in various dielectric materials have been investigated in detail.^{3–5} Indium oxide (In₂O₃) is a wide-bandgap semiconductor $(E_g = 3.75 \text{ eV})^{6-10}$ that has been subjected to extensive study on account of its versatility in applications such as solar cells, 11 gas sensors, 12 and fieldemission displays.¹³ The visible-light emission properties of In₂O₃ correlated with defect levels in the bandgap have been reported by various research groups. 6,14,15 Mazzera *et al.* observed three emission bands with peaks located at 454, 563, and 631 nm in the cathodoluminescence spectra of In₂O₃ samples.⁶ Photoluminescence (PL) signals at 429, 460, and 637 nm were reported by Zheng *et al.*¹⁴ and Lee *et al.*¹⁵ during their studies on In₂O₃ in nanowire and thin-film forms, respectively. However, previous studies mainly investigated samples containing pristine In₂O₃, and the debate concerning the emission mechanism is ongoing. For instance, Orlandi et al. 16 and Franceschetti and Zunger 17 reported that the visible-light emissions are related to oxygen defects. Kumar et al. found that In; is responsible for the red emission. 18 Brus¹⁹ and Yoshimura et al.²⁰ attributed the blue-green emissions to the transitions correlated with oxygen defects. Since oxygen defect levels are unlikely to split into such a wide range in the bandgap of In₂O₃, further study is hence required. In addition to modulating the defect types and populations in In₂O₃ nanoparticles, this work also investigates the dielectric confinement effect by adding nitrogen (N) elements

in the nanocomposite thin films containing In_2O_3 nanoparticles so as to clarify the luminescence mechanisms.

The dielectric confinement effect may occur in nanocomposite thin films containing discrete semiconductor QDs owing to the presence of surface polarizations. ^{16–18} Such polarizations are induced by charge accumulation on the particle surface when the dielectric mismatch presents at the QD/matrix interface. It consequently causes the confinement of electron states, and thus the dielectric confinement effect in the samples. ^{19–21} Because of the large specific surface area (SSA) feature of QDs, the surface states of QDs greatly affect the physical properties of nanocomposite thin films, resulting in distinctive optical and electrical properties. ^{22–24}

In this study, the N-incorporated nanocomposite thin films containing In_2O_3 nanoparticles embedded in a SiO_2 matrix are prepared by utilizing InN pellets and allowing N_2 inlet gas flow during the target-attachment sputtering process. The PL properties of samples are measured and compared with those of N-free samples in order to clarify the role of defect levels and the dielectric confinement effect on the emission properties. The microstructures and compositions of nanocomposite samples are analyzed by transmission electron microscopy (TEM) and *x*-ray photoelectron spectroscopy (XPS), respectively. Their correlations to the PL properties are discussed in order to clarify the possible origins of visible-light emissions of In_2O_3 proposed previously.

II. EXPERIMENT

Nanocomposite thin films containing In_2O_3 nanoparticles embedded in a SiO_2 matrix were prepared using the target-attachment method 10,25 in a sputtering system with background pressure better than $10^{-7}\,\mathrm{Torr}$. For the samples containing pristine In_2O_3 nanoparticles, various quantities of In_2O_3 pellets were mounted on a quartz target and radio-frequency (RF) magnetron sputtering deposition was then

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TABLE I. A list of sample designation, sputtering conditions, $\rm In_2O_3$ nanoparticle diameters, and N contents of nanocomposite thin films.

	Sputtering con	ditions			
Sample designation	Pellet type/Number	N ₂ /Ar ratio	Particle diameter (nm)	N content (at. %)	
a	In ₂ O ₃ /1	0	3.1	0	
b	In ₂ O ₃ /1	0.05	3.2	0.5	
c	$In_2O_3/1$	0.15	3.7	1.4	
d	In ₂ O ₃ /1	0.25	3.7	1.8	
e	InN/1	0.05	3.6	0.5	
f	InN/1	0.15	3.8	2.3	
g	InN/1	0.25	3.6	2.9	
h	InN/3	0.05	3.8	1.0	
i	InN/3	0.15	3.5	3.6	
j	InN/3	0.25	3.7	4.5	

carried out at a gun power of $130\,\mathrm{W}$ and a working pressure of $3.5\,\mathrm{mTorr}$ with high-purity argon (Ar) as the inlet gas flow. The nanoparticle content in the samples was adjusted by varying the number of $\mathrm{In_2O_3}$ pellets. For the N-incorporated samples, a mixed $\mathrm{N_2/Ar}$ inlet gas flow at various ratios of 5% to 25% (in standard cubic centimeters per minute) was

introduced during the sputtering. Moreover, InN pellets, instead of pure In_2O_3 pellets, were chosen as the source of In_2O_3 nanoparticles in these samples. As revealed by subsequent XPS analysis, the InN transforms into N-incorporated In_2O_3 with a composition in the form of InO_xN_y . This was ascribed to the enrichment of oxygen (O) elements in the SiO_2 matrix, which in turn caused the oxidation of InN. The addition of N_2 inlet gas flow during sputtering further increased the N content of the samples, amplifying the dielectric confinement effect on the emission properties of the nanocomposite samples. Sample designations and corresponding preparation conditions are listed in Table I.

The PL properties, microstructures, and compositions of the samples were characterized immediately after the completion of sample preparation. No post-annealing treatment was performed to modulate the structures and properties of samples. The microstructures of the nanocomposite thin films were examined by TEM (JEOL, JEM-2100F) operated at 200 kV. The evolution of the chemical bonds of the elements in the samples was analyzed by XPS (American Physical Electronics ESCA PHI 1600) using Mg- K_{α} x-ray excitation. The PL spectra of the samples were measured at room temperature using a self-assembly PL apparatus equipped with a 325-nm He-Cd laser.

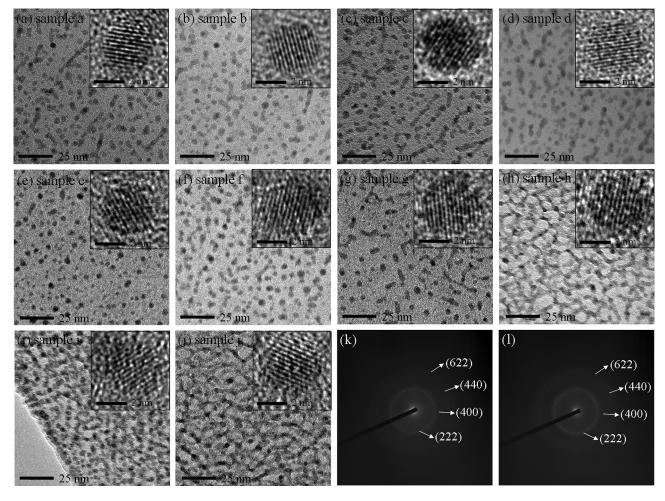


FIG. 1. TEM images (a) to (j) show the microstructures corresponding to samples a-j. Inset at the upper right-hand corner of each micrograph is the high-magnification images of nanoparticles. Typical SAED patterns of nanocomposite thin films prepared by using In_2O_3 and InN pellets are separately given in (k) and (l). The indices of SAED patterns according to JCPDS standard No.06-0416 indicated the phase type of nanoparticles is In_2O_3 regardless of the pellet type employed during sputtering deposition.

III. RESULTS AND DISCUSSIONS

A. Microstructures

Figures 1(a)-1(j) separately present the TEM micrographs of nanocomposite samples a-j. Inset at the upper right-hand corner of each micrograph is an enlarged image of the nanoparticles embedded in each of the samples; a single set of lattice fringes presenting the nanoparticle reveals

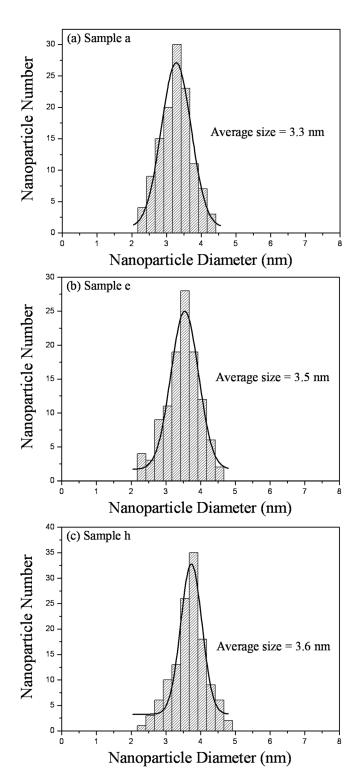


FIG. 2. The histograms of particle size distribution for samples (a) a, (b) e, and (c) h.

the single crystalline form of the nanoparticles. Typical selected area electron diffraction (SAED) patterns for the samples prepared using $\rm In_2O_3$ and InN pellets are shown in Figs. 1(k) and 1(l), respectively. The indices of the SAED patterns indicate that the phase type of the nanoparticles is body-centered cubic (BCC) $\rm In_2O_3$, regardless of the pellet type used for sample preparation. The hexagonal InN phase was not detected in all samples; however, subsequent XPS analysis revealed the presence of N elements in the $\rm In_2O_3$ nanoparticles. The absence of the InN phase indicates that InN transforms to N-incorporated $\rm In_2O_3$, the result of an oxidation reaction because it was embedded in the $\rm SiO_2$ matrix with many O elements.

InN tends to decompose at high temperatures, reportedly at temperatures higher than $550\,^{\circ}\text{C}$. The decomposition temperature of InN might be reduced in an environment with a low N_2 gas partial pressure and in our samples, the residual In elements might react with the surrounding to form In_2O_3 as follows: 27,28

$$InN_{(s)} = In_{(s)} + \frac{1}{2}N_{2(g)},$$

$$4In_{(s)} + 3O_{2(g)} = 2In_2O_{3(s)}.$$

The instability of InN can also be understood by the fact that the heat of formation for InN $(34\,\text{kcal/mole})^{29}$ is much lower than that of In_2O_3 (221 kcal/mole).³⁰ The instability and subsequent oxidation of InN might thus result in N-incorporated In_2O_3 nanoparticles in the nanocomposite samples prepared using the InN pellets.

The average nanoparticle diameters of each sample were also calculated by measuring the sizes of at least 110 nanoparticles in each TEM image; the results are summarized in Table I. The representative histograms of particle size distribution for samples a, e, and h are shown in Figs. 2(a)–2(c). Note that all samples were prepared at the same RF gun power of 130 W, yielding nanoparticles of similar size. Moreover, in order to avoid the influence of the

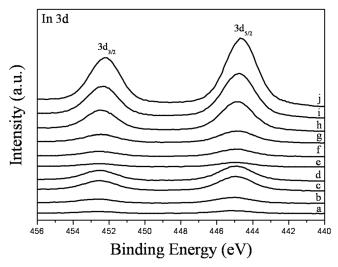


FIG. 3. In 3d XPS spectra for nanocomposite samples containing $\rm In_2O_3$ nanoparticles.

quantum confinement effect, we prepared nanoparticles with sizes larger than the Bohr radius of $\rm In_2O_3$ (i.e., $1.32\,\rm nm$). Calibration indicated that the diameters of the $\rm In_2O_3$ nanoparticles were in the range of 3.2 to 3.7 nm (i.e., the radius range of 1.6 to 1.85 nm) as listed in Table I. This is suitable for discussing the N-incorporation effects in nanocomposite thin films containing $\rm In_2O_3$ nanoparticles.

B. XPS analysis

The N contents of nanocomposite samples were calibrated in terms of the XPS analytical results and are summarized in Table I. It can be seen that the N content of sample increases with an increasing number of InN pellets and an increasing N_2/Ar inlet gas flow ratio. However, the values

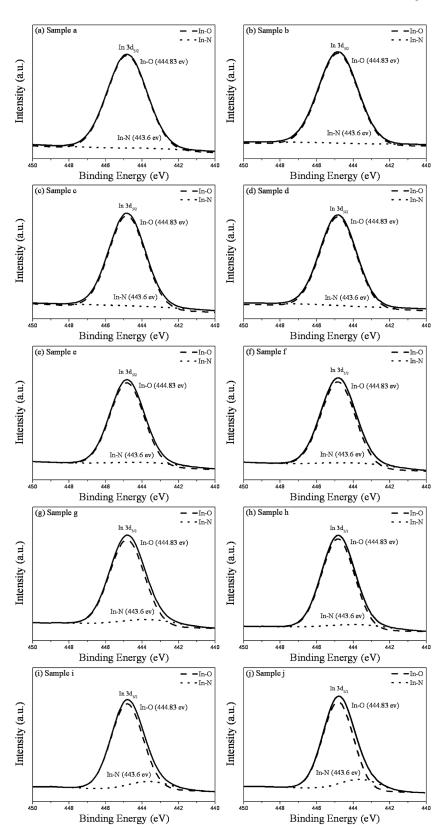


FIG. 4. In $3d_{5/2}$ XPS spectra and corresponding curve fitting results for samples a to j.

TABLE II. Summary of XPS information and curve fitting results for the nanocomposite samples containing In₂O₃ nanoparticles.

	XPS integrated intensity ratio (%)							
	In 3d _{5/2}	O 1s			N 1s			
Sample	In-N bond	O _{lattice}	O ⁻	O ²⁻	Si-O-N bond	In-O-N bond		
а	_	1.86	30.4	67.7	_	_		
b	_	3.12	38.7	58.1	_	_		
c	_	4.48	47.7	47.8	_	_		
d	_	5.64	52.5	41.8	_	_		
e	7.9	4.63	53.9	41.4	84.9	15.1		
f	8.7	4.84	55.2	40.0	82.1	17.9		
g	10.7	6.63	60.7	32.6	75.3	24.7		
h	8.9	7.73	53.4	38.9	81.2	18.8		
i	10.1	8.83	57.5	33.6	75.1	24.9		
j	13.7	12.5	59.6	27.9	66.1	33.9		

listed in Table I represent the overall N contents of the nanocomposite samples, rather than that of In₂O₃ nanoparticles or the SiO₂ matrix. Hence, the evolution of the In-N bond was further analyzed by XPS in order to discriminate the N contents in In₂O₃ nanoparticles.

Figure 3 depicts the In 3d XPS spectra for various nanocomposite samples. A slight shift of the In 3d XPS peaks toward the low bonding energy side can be seen for the samples prepared using InN pellets and high N₂/Ar gas flow ratios. With the knowledge of the In-N bonding energy (i.e., 443.6 eV), ³² deconvolution of the In $3d_{5/2}$ XPS profiles was performed using the Gaussian curve-fitting method,³³ and the results for each sample are separately presented in Figs. 4(a)-4(j). As shown by Figs. 4(a)-4(d), the In-N signals are negligibly small for samples a-d, which were prepared using In₂O₃ pellets. Hence, the incorporation of N₂ gas during sputtering barely facilitated the formation of In-N bonds in In₂O₃ nanoparticles. Subsequent XPS analysis revealed that the N₂-gas incorporation during sputtering in fact mainly modifies the SiO₂ matrix by eliminating oxygen defects and resulting in the Si-O-N bond. For samples e-j, the XPS peak corresponding to the In-N bond emerges, and its intensity increases with an increasing number of InN pellets. The percentages of In-N bond contents were calibrated in terms of the integrated intensity ratios of deconvoluted XPS profiles, as shown in Figs. 4(e)-4(j), and the results are listed in Table II. This illustrates that the N-incorporated In₂O₃ QDs can be realized by using InN pellets for sputtering deposition of nanocomposite samples.

Figures 5(a)-5(j) present the O 1s XPS spectra and corresponding curve-fitting results for samples a-j. All O 1s XPS spectra can be deconvoluted into three components: Olattice (the lattice oxygen in the In₂O₃ lattice; at about 530.2 eV), O (the oxygen ions at the nanoparticle surface; at about 531.8 eV), and O^{2-} (the oxygen vacancies in the SiO₂ matrix and In₂O₃ nanoparticles, or the partially weakly adsorbed oxygen species, at about 532.7 eV). Table II summarizes the percentages of the O²⁻ component and the In-O-N content for each of the nanocomposite samples, deduced by the ratios of the integrated intensities of deconvoluted XPS profiles as shown in Figs. 5(a)-5(j). Sample a, prepared without N2-gas incorporation, contains many oxygen defects, as indicated by its high O^{2-} content of 66.7%. With increasing N₂/Ar inlet gas flow ratio, the percentage of the O²⁻ component decreases from 58.1% to 41.8% for samples b-d, prepared with N2-gas incorporation. In conjunction with the analytical results of In 3d XPS spectra presented above, this implies that the N₂-gas incorporation may effectively eliminate oxygen defects in the SiO2 matrix of nanocomposite samples. Further suppression of the O²⁻ component can be seen in samples e-j, prepared using InN pellets. The formation of In-N bonds in nanoparticles may simultaneously improve their crystallinity.

Figure 6 presents the N 1s XPS spectra and corresponding curve-fitting results for samples a-j, calibrated in terms of the bonding energies for Si-O-N bonds (397.4-398.4 eV) and In-O-N bonds (396.4 eV). 34 According to these deconvoluted profiles, the integrated intensity ratios of Si-O-N and In-O-N bonds in samples a-j were calculated, and the results are listed in Table II. As shown in Fig. 6 and Table II, the In-O-N signal emerges only in samples e-i, prepared using InN pellets, and its intensity increases with an increasing number of InN pellets. Moreover, the peak of the N 1s core level was found to be located at 396.4 eV, indicating that the N atoms mainly occupy the oxygen vacancy sites rather than the interstitial sites in the In₂O₃ lattice. ^{34,35} This is in agreement with the analytical result of the O 1s XPS spectra, which indicates the suppression of the O²⁻ component in samples e-j. On the other hand, the presence of a Si-O-N component in all samples indicates the formation of SiO_xN_y in the SiO_2 matrix on account of the incorporation of N₂ gas during sputtering.

C. Luminescence properties and the origins of visible-light emissions

Figure 7 shows the PL spectra of nanocomposite thin films containing In₂O₃ nanoparticles measured in the wavelength range of 350 to 750 nm. Since the E_g of In_2O_3 is 3.75 eV (i.e., 330 nm), the PL emissions shown in Fig. 8 should correlate to either the carrier recombination between the conduction band (CB) edge and defect levels and/or between the defect levels and the valence band (VB) edge. Figures 8 and 9 present the curve-fitting results of the PL spectra corresponding to the samples prepared using the In₂O₃ and InN pellets, respectively. As shown in Fig. 8, the PL spectra of samples a-d are comprised of three emission bands, i.e., red, green, and blue emissions. The integrated intensity ratio of green emission decreases with increasing N content in the samples. As indicated in Table III, the integrated intensity ratio decreases from 35.3% to 30.3%. The above-presented XPS analysis indicates that N2-gas incorporation mainly affects the composition of the SiO₂ matrix. Hence, the surface polarization effect, induced by the formation of a SiO_xN_y phase in the SiO₂ matrix, should be considered in interpreting the PL properties of samples a-d. Note that the quantum confinement effect is not considered here since the radii of the In₂O₃ nanoparticles in all samples (1.55 to 1.9 nm) are larger than the Bohr radius of In₂O₃ (i.e.,

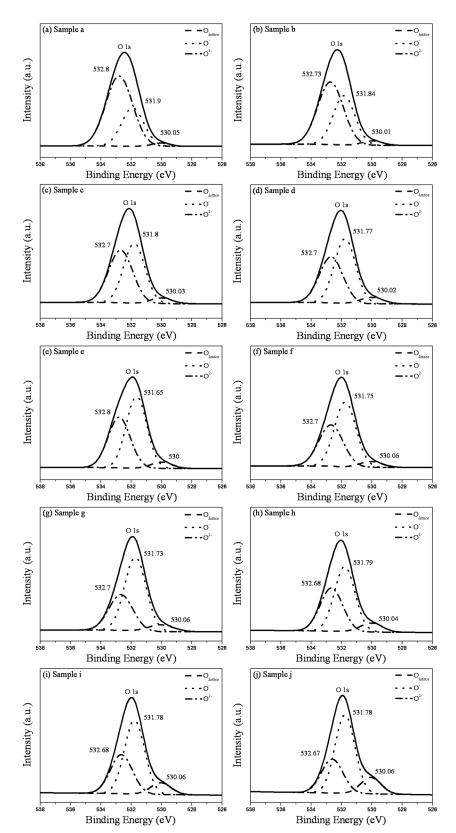


FIG. 5. O 1s XPS peaks and corresponding curve fitting results for samples a to j.

1.32 nm), as indicated by the particle size measurement results presented in Table I. Moreover, our previous study³¹ reported that the quantum confinement effect mainly causes a blue shift of emission peaks, rather than a relative intensity change between different emissions. This is further illustrated by the PL spectra shown in Figs. 10(a) and 10(b), which depict the peak locations at 340–343 nm, i.e., the

difference in E_g between the samples is merely 0.03 eV. This implies that the quantum confinement effect is negligible on the PL performance of the samples prepared in this study. Figures 11(a) and 11(b) present the bonding configuration models at the interfaces of the In_2O_3 nanoparticle/SiO₂ matrix and the In_2O_3 nanoparticle/SiO_xN_y matrix, respectively. In the In_2O_3 -SiO₂ system, the O⁻ species might react with

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FIG. 6. N 1s XPS spectra and corresponding curve fitting results for samples a to j.

the (SiO_4) units in the SiO_2 matrix to form O-Si bonds on the nanoparticle surface. However, it is in the direction opposite to the Si-O bonds in the SiO_2 matrix, leaving a relatively weak surface polarization at the nanoparticle/matrix interface in the In_2O_3 QDs-SiO₂ system. ³⁶ On the contrary, both

the dipole moments resulting from the $O(\delta^-)$ - $N(\delta^+)$ and N-Si bonds contribute to the effective polarization toward the nanoparticle surface in the In_2O_3 -SiO $_xN_y$ system. The formation of the SiO_xN_y phase in the SiO_2 matrix therefore enhances the surface polarization, causing the dielectric

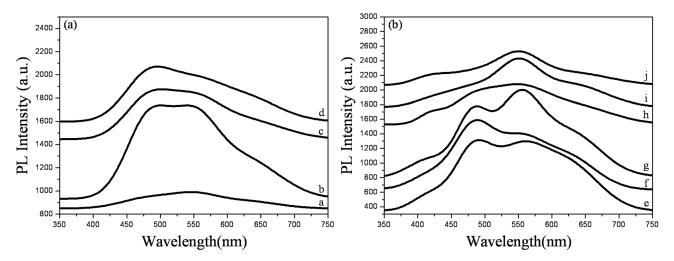


FIG. 7. PL spectra of nanocomposite samples (a) a to d prepared by using the In₂O₃ pellets and (b) e to j prepared by using the InN pellets.

confinement effect and consequently discouraging carrier transport in the samples. 36,37

In the samples containing nanoscale particles, the band bending effect would generate surface and volume states due to hole migration toward the nanoparticle surface 38,39 and electron migration toward the nanoparticle interior, 40,41 respectively. A previous study found that the green emissions of In_2O_3 QD-SiO₂ nanocomposite layers are correlated

to hole-related defect levels or acceptor-type defects, such as $V_{In}^{\prime\prime\prime}^{10}$. Figure 8 and Table III depict the decrease of green emission with the increase of nitridation in the SiO₂ matrix of samples a-d, illustrating that the dielectric confinement effect indeed affects the physical properties relating to the surface states of nanoparticles. This also confirms that the green emission of nanocomposite thin films containing In₂O₃ nanoparticles originates from the acceptor defect $V_{In}^{\prime\prime\prime}$.

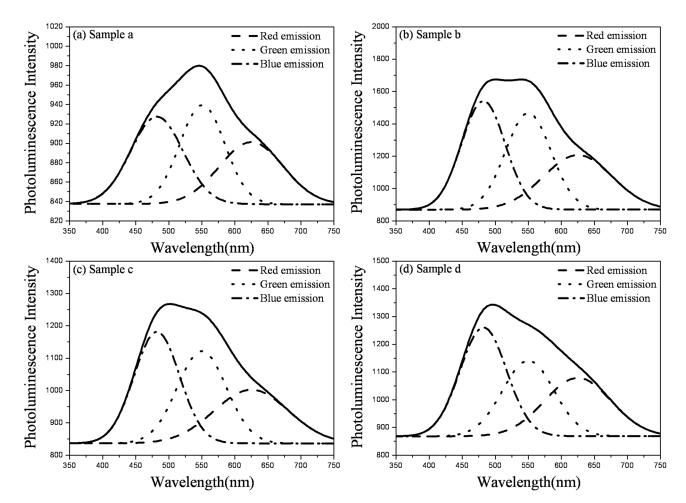


FIG. 8. Curve fitting results for PL spectra for nanocomposite samples a to d prepared by using the In₂O₃ pellet.

TABLE III. Summary of curve fitting results of PL spectra for the nanocomposite samples containing In₂O₃ nanoparticles.

Sample	PL peak position (nm)			PL integrated intensity ratio (%)				
	Red	Green	Blue	Violet	Red	Green	Blue	Violet
a	625	550	482	418	30.6	35.3	34.2	_
b	625	550	482	418	29.1	34.0	36.9	_
c	625	550	482	418	29.4	33.4	37.2	_
d	625	550	482	418	30.3	30.3	39.4	_
e	625	550	482	418	33.8	34.2	27.5	4.5
f	625	550	482	418	33.5	35.4	26.5	4.7
g	625	550	482	418	34.9	36.4	23.4	5.4
h	625	550	482	418	35.7	32.7	26.6	5.1
i	625	550	482	418	36.9	33.5	24.0	5.6
j	625	550	482	418	38.2	34.5	21.0	6.4

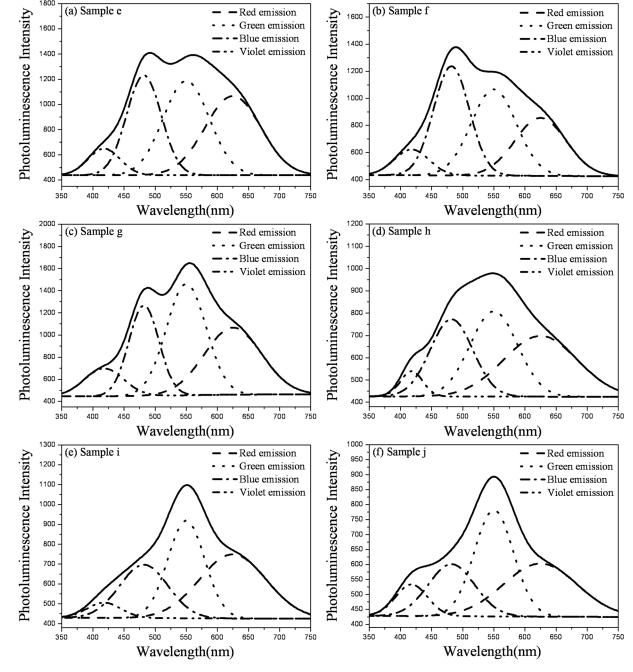


FIG. 9. Curve fitting results for PL spectra for nanocomposite samples e to j prepared by using the InN pellet.

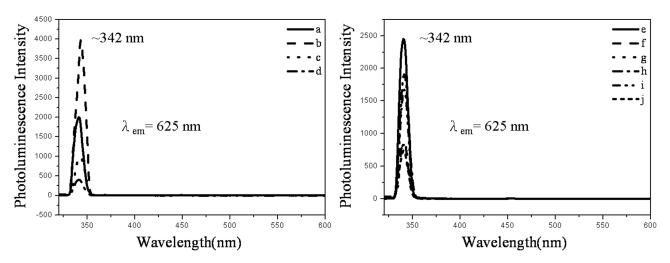


FIG. 10. PLE spectra of nanocomposite samples (a) a to d prepared by using the In₂O₃ pellets and (b) e to j prepared by using the InN pellets.

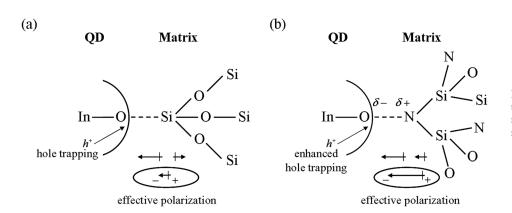


FIG. 11. Bonding configuration models at the interfaces of (a) In_2O_3 nanoparticle/SiO₂ matrix and (b) In_2O_3 nanoparticle/SiO_xN_y matrix.

In the PL spectra of samples *e-j* prepared using InN pellets, a violet emission at 418 nm emerges in addition to the red, green, and blue emissions, as shown by their deconvolution profiles in Figs. 9(a)-9(f). The violet emission of In_2O_3 was also reported by Kundu and Biswas,42 who attributed the emission to the excitonic emission of In₂O₃ because the shift of violet emission with the variation of excitation energy was observed. However, according to the XPS results and PL properties of samples a-d presented above, the violet emission should correlate with the incorporation of N elements in In₂O₃ nanoparticles. As listed in Table II, the integrated intensity ratios of emissions deduced from the PL spectra of samples e-i indicate that the intensity ratio of violet emissions increases with the increase of In-O-N bonds and vice versa for blue emission. It is inferred that an extra defect level is generated by the occupancy of N elements in oxygen sites, i.e., N_0^- in N-incorporated In₂O₃ nanoparticles, and the transition from CB to such a defect level may be responsible for the violet emission. As for the blue emission, N₂-gas incorporation during sputtering may eliminate the oxygen vacancies in the oxide, 43 and previous XPS analysis indicates the suppression of the O^{2-} component in samples e-i when the N content is increased. The decrease of blue emissions in samples e-j should thus correlate to the elimination of oxygen vacancies in the nanoparticles. This further confirms the assignment of the blue emission to the transition from the CB edge to oxygen defect levels of the In_2O_3 , as reported in previous studies.

IV. CONCLUSIONS

In this study, we prepared nanocomposite thin films containing In₂O₃ nanoparticles using the target-attached sputtering method, utilizing InN pellets and allowing N2 inlet gas flow during the deposition process. The influence of the dielectric confinement effect on the emission properties of the samples was characterized in order to clarify the debates on the emission mechanisms of In₂O₃. TEM analysis revealed that single-crystalline In₂O₃ nanoparticles were well dispersed in the SiO₂ matrix, and that the In₂O₃ is of the BCC phase type. Utilization of InN pellets for sample preparation did not imply the existence of InN nanoparticles in the samples; this was attributed to the oxidation of the InN phase as it was embedded in the SiO2 matrix enriched with O elements. XPS analysis revealed that the composition of In₂O₃ nanoparticles is, in fact, in the form of InO_xN_y , and the SiO_xN_y phase is observed in the SiO_2 matrix due to the N_2 gas incorporation during sputtering deposition. Nitridation in the SiO_2 matrix induced the dielectric confinement effect and restrained the green emission of samples due to the enhancement of polarization on the In_2O_3 nanoparticle surface. Moreover, the N_2 -gas incorporation reduced the oxygen vacancies in the In_2O_3 and consequently suppressed the blue emission of samples. Violet emissions were observed in the samples prepared using InN pellets, and were correlated to a new defect level, N_O^- , resulting from the substitution of N elements in oxygen lattice sites. The analytical results presented above confirm the mechanisms of visible-light emissions of In_2O_3 nanoparticles reported previously. 10

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