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LETTER

Theoretical analysis on yellow emission of gallium nitride with vacancy defects or impurities

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Abstract The absorption and the emission spectra of wurtzite GaN with some vacancy defects or impurities (V_{Ga}, V_{Ga}–O_N, V_{Ga}–H, V_N, V_N–H, C_{Ga}, C_N, $C_{i,}$ Si_{Ga}, O_N) were calculated by using TDDFT method with cluster models. $Ga_{26}N_{26}H_{50}$ cluster is chosen as a basic cluster according to the predicted energy gap. The TD-B3LYP calculation results show that yellow emission of about 2.2 eV of GaN material attributes to the presence of V_{Ga}–O_N complex. The other vacancy defects or impurities bring out emission of about 2.0–2.1 eV or have no effect on yellow emission of GaN.

Keywords Gallium nitride · Vacancy defects and impurities · TDDFT · Optical property · Yellow emission

1 Introduction

Gallium nitride (GaN) is one of the ideal materials suitable for blue, green and UV optical devices that can be applied in optical memory, high frequency and high power display, ocean communication and so on [1, 2]. Some vacancy defects or impurities in the as-grown GaN material often arouse yellow emission to reduce the efficiency of blue emission. At present, many theoretical and experimental researches on the yellow emission of GaN [3–19] consider this emission to peak at 2.2 eV and the transition to be related to defect levels. However, there is no verdict for the idiographic reason of the yellow emission and the different viewpoints are as follows. The first viewpoint is that gallium vacancy (V_{Ga}) [3–6] or nitrogen vacancy (V_N) [7] arouses yellow emission. The growth dynamics determines the presence of this type of vacancy defects for the N-rich case or the Ga-rich case. The second viewpoint is with respect to hydrogen-related complexes. Hydrogen is abundantly present in GaN material that is grown by the MOCVD or HVPE process. It should be bound to a Ga vacancy or N vacancy to form stable complexes (V_{Ga}–$H_{1–4}$ or V_N–H) [8]. The third viewpoint considers carbon-intentional dopant as an important reason [6, 9–11]. The fourth one deals with silicon impurity (Si_{Ga}) [12–15]. In the experiment, silicon is a common unintentional impurity, which comes from raw material contaminated by Si or quartz glass reactor under high temperature. The last viewpoint considers oxygen impurity as being unintentionally ubiquitous for most semiconductors, since oxygen is often present in the growth environment. A prevailing viewpoint is that the complex of gallium vacancy and O impurity (V_{Ga}–O_N) is mainly responsible for yellow emission [16–19]. In order to confirm the main reason of yellow emission in this work, the time-dependent density functional theory (TDDFT) method [20–24] will be employed to analyze the spectrum character of the wurtzite-type GaN with vacancy defect or impurity by using the cluster model.

2 Computational details

According to a study [25], the position of the absorption peak varies depending on the cluster geometry chosen. Energy gap is an important factor for the spectrum

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property. So, cluster geometry could be chosen according to energy gap. In this paper, the compositions of Ga_4N_4, $Ga_{13}N_{13}$, $Ga_{26}N_{26}$ and $Ga_{39}N_{39}$ are chosen as GaN cluster model and hydrogen atoms to saturate the dangling bonds at the boundary of the cluster (Fig. 1). The structures of the latter three clusters are consistent with that of single wurtzite cell. The energy gaps of four clusters were computed by Becke's three-parameter hybrid functionals (B3LYP) and the corresponding results are 6.90, 4.31, 3.35 and 3.33 eV, respectively. This is a consequence of the quantum size effect. Therefore, the energy gap of $Ga_{26}N_{26}$ and $Ga_{39}N_{39}$ clusters are closest to the calculated energy gap (3.52 eV) predicted using the B3LYP hybrid functional [26] and is in good agreement with the experimental band gap value (3.4 eV [1]) of bulk GaN. However, it needs a much longer time to compute for the $Ga_{39}N_{39}$ cluster. So, $Ga_{26}N_{26}$ cluster is chosen as a basic cluster and the considered vacancy defect or impurity, such as V_{Ga}, V_{Ga}–O_N, V_{Ga}–H, V_N, V_N–H, C_{Ga}, C_N, C_i, Si_{Ga} or O_N, is arranged in the central section.

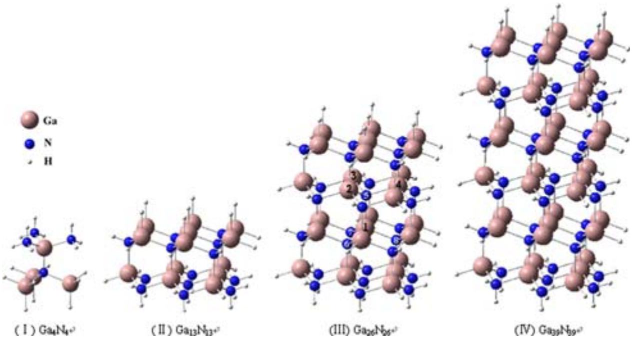


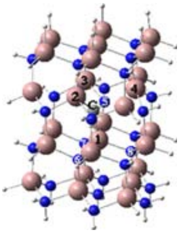
Fig. 1 Cluster models of GaN for theoretical computation

In the calculation, Hay and Wadt's relativistic effective core potentials (RECPs) were adopted for Ga atoms, in which 28 electrons were incorporated into pseudopotentials. A (6s6p/3s3p) basis set was employed for Ga atoms around the vacancy defect or impurity site and a (3s3p/1s1p) basis set for the other Ga atoms. The standard 6-31G basis sets were chosen for N atoms closest to the vacancy defect or impurity site and impurity atoms, while 3-21G basis sets were used for the rest of the N atoms and all H atoms. The structural optimizations for the clusters at the ground state were performed by Becke's three-parameter hybrid functionals (B3LYP), and the absorption spectra of the clusters were calculated by using the TDDFT method. Moreover, single configuration interaction (CIS) method was adopted to optimize the structure of the singlet excited state of the clusters, and then the emission spectra were obtained by the TD-B3LYP method [20–23]. In this stage, all calculations for the cluster models were performed with Gaussian 03 package.

3 Results and discussion

Bond lengths of the optimized structure in the central section of the clusters are shown in Table 1. The bond lengths between the vacancy defect and the conjoint atom

Table 1 Bond length of the optimized structure and C_i:GaN cluster inset

Bond length (nm)					
GaN	V_{Ga}:GaN	V_{Ga}–O_N:GaN	V_{Ga}–H:GaN	V_N:GaN	V_N–H:GaN
$R_{Ga(1)\text{-}N(6)} = 0.1988$	$R_{VGa\text{-}N(6)} = 0.2534$	$R_{VGa\text{-}N(6)} = 0.2547$	$R_{H(1)\text{-}N(6)} = 0.1035$	$R_{Ga(1)\text{-}N(6)} = 0.2026$	$R_{Ga(1)\text{-}N(6)} = 0.2050$
$R_{Ga(1)\text{-}N(7)} = 0.1990$	$R_{VGa\text{-}N(7)} = 0.2539$	$R_{VGa\text{-}N(7)} = 0.2547$	$R_{H(1)\text{-}N(7)} = 0.3012$	$R_{Ga(1)\text{-}N(7)} = 0.2038$	$R_{Ga(1)\text{-}N(7)} = 0.2069$
$R_{Ga(1)\text{-}N(8)} = 0.1990$	$R_{VGa\text{-}N(8)} = 0.2534$	$R_{VGa\text{-}N(8)} = 0.2547$	$R_{H(1)\text{-}N(8)} = 0.3010$	$R_{Ga(1)\text{-}N(8)} = 0.2037$	$R_{Ga(1)\text{-}N(8)} = 0.2069$
$R_{Ga(1)\text{-}N(5)} = 0.1887$	$R_{VGa\text{-}N(5)} = 0.2291$	$R_{VGa\text{-}ON(5)} = 0.2272$	$R_{H(1)\text{-}N(5)} = 0.2790$	$R_{Ga(1)\text{-}VN} = 0.1945$	$R_{Ga(1)\text{-}H(5)} = 0.2650$
$R_{N(5)\text{-}Ga(2)} = 0.1976$	$R_{N(5)\text{-}Ga(2)} = 0.1989$	$R_{O(5)\text{-}Ga(2)} = 0.1885$	$R_{N(5)\text{-}Ga(2)} = 0.1975$	$R_{VN\text{-}Ga(2)} = 0.2156$	$R_{H(5)\text{-}Ga(2)} = 0.2782$
$R_{N(5)\text{-}Ga(3)} = 0.1977$	$R_{N(5)\text{-}Ga(3)} = 0.1992$	$R_{O(5)\text{-}Ga(3)} = 0.1890$	$R_{N(5)\text{-}Ga(3)} = 0.1973$	$R_{VN\text{-}Ga(3)} = 0.2150$	$R_{H(5)\text{-}Ga(3)} = 0.1738$
$R_{N(5)\text{-}Ga(4)} = 0.1977$	$R_{N(5)\text{-}Ga(4)} = 0.1993$	$R_{O(5)\text{-}Ga(4)} = 0.1890$	$R_{N(5)\text{-}Ga(4)} = 0.1973$	$R_{VN\text{-}Ga(4)} = 0.2151$	$R_{H(5)\text{-}Ga(4)} = 0.1741$
C_{Ga}:GaN	C_N:GaN	C_i:GaN		Si_{Ga}:GaN	O_N:GaN
$R_{C(1)\text{-}N(6)} = 0.2661$	$R_{Ga(1)\text{-}N(6)} = 0.2008$	$R_{Ga(1)\text{-}N(6)} = 0.1966$		$R_{Si(1)\text{-}N(6)} = 0.1857$	$R_{Ga(1)\text{-}N(6)} = 0.1937$
$R_{C(1)\text{-}N(7)} = 0.2649$	$R_{Ga(1)\text{-}N(7)} = 0.2001$	$R_{Ga(1)\text{-}N(7)} = 0.1938$		$R_{Si(1)\text{-}N(7)} = 0.1844$	$R_{Ga(1)\text{-}N(7)} = 0.1935$
$R_{C(1)\text{-}N(8)} = 0.1461$	$R_{Ga(1)\text{-}N(8)} = 0.2001$	$R_{Ga(1)\text{-}N(8)} = 0.2022$		$R_{Si(1)\text{-}N(8)} = 0.1857$	$R_{Ga(1)\text{-}N(8)} = 0.1932$
$R_{C(1)\text{-}N(5)} = 0.1337$	$R_{Ga(1)\text{-}N(5)} = 0.1909$	$R_{Ga(1)\text{-}N(5)} = 0.2186$		$R_{Si(1)\text{-}N(5)} = 0.1796$	$R_{Ga(1)\text{-}O(5)} = 0.1966$
$R_{N(5)\text{-}Ga(2)} = 0.2277$	$R_{C(5)\text{-}Ga(2)} = 0.1945$	$R_{Ci\text{-}Ga(1)} = 0.1943$		$R_{N(5)\text{-}Ga(2)} = 0.2088$	$R_{O(5)\text{-}Ga(2)} = 0.2078$
$R_{N(5)\text{-}Ga(3)} = 0.2265$	$R_{C(5)\text{-}Ga(3)} = 0.1962$	$R_{Ci\text{-}Ga(2)} = 0.2076$		$R_{N(5)\text{-}Ga(3)} = 0.2092$	$R_{O(5)\text{-}Ga(3)} = 0.2082$
$R_{N(5)\text{-}Ga(4)} = 0.2129$	$R_{C(5)\text{-}Ga(4)} = 0.1962$	$R_{Ci\text{-}N(5)} = 0.1339$		$R_{N(5)\text{-}Ga(4)} = 0.2089$	$R_{O(5)\text{-}Ga(4)} = 0.2078$

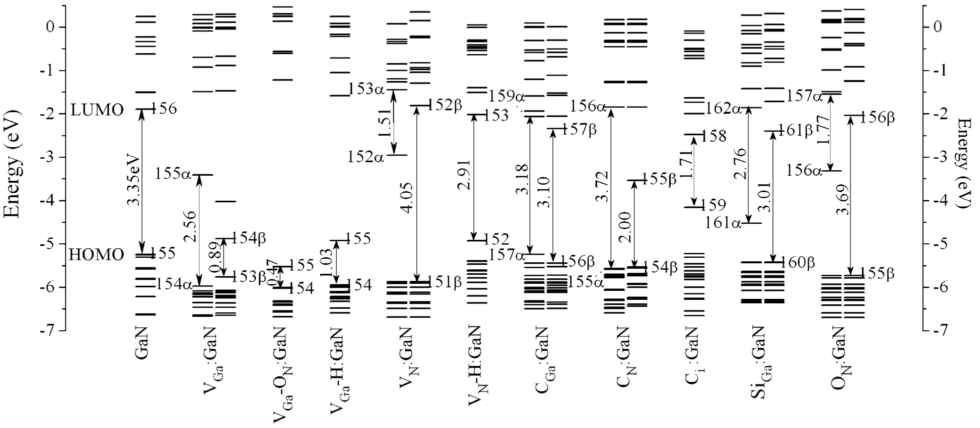


Fig. 2 Arrangement of the front molecule orbits at the ground state

almost increase. For the impurity with smaller radius, such as C_{Ga}, the correlative bond lengths change obviously. Based on the optimized structure of the ground state, the arrangements of the front molecular orbitals (MOs) of the GaN cluster and the clusters with vacancy defect or impurity (Fig. 2) can be calculated by the TDDFT method. The energy gaps of the clusters with vacancy defect or impurity are smaller due to the presence of new levels.

According to the calculated vertical absorption excitation energy and oscillator strength (*f*), the absorption spectra of these clusters can be simulated by Gaussian fitting method and are shown in Fig. 3. The absorption of $Ga_{26}N_{26}$ cluster in the region of visible light is weak. Its minimal vertical excitation energy is 2.95 eV and the corresponding absorption band peaks at 3.09 eV. When vacancy defects or impurities are included in the clusters, the new energy levels appearing in the gap result in a decrease in the lowest threshold of the excitation energy. The strong absorption bands are shown in Fig. 3. Since the absorption band of V_{Ga}–H:GaN, V_N:GaN, V_N–H:GaN, C_{Ga}:GaN or Si_{Ga}:GaN, of about 3.7 eV, is strong, these vacancy defects or impurities may have an effect on the absorption efficiency of GaN material from excitation light of about 330 nm.

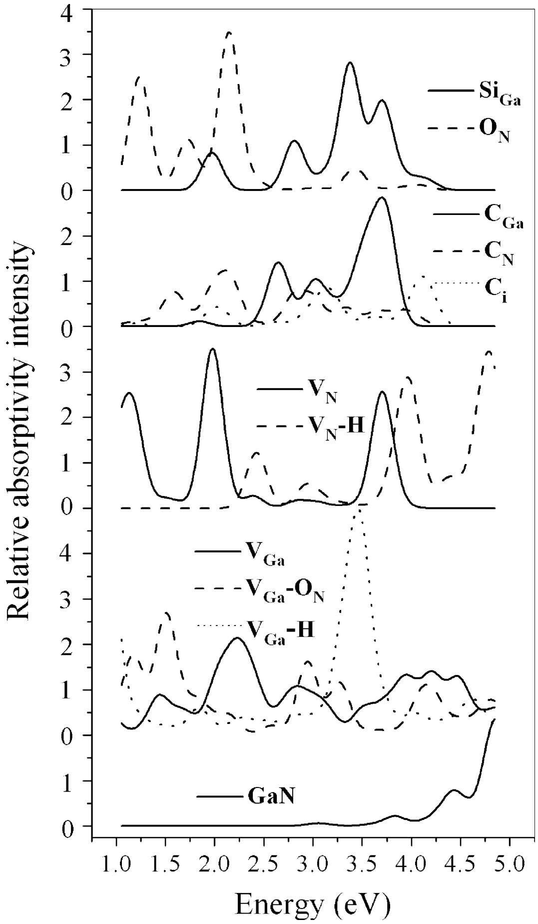


Fig. 3 Absorption spectra of GaN clusters calculated by the TDDFT method

After determining the configuration of the singlet excited state by the CIS method, the emission spectra of $Ga_{26}N_{26}$ cluster and the clusters with vacancy defect or impurity were calculated by the TDDFT method [20–23]. Some results, such as the vertical emission excitation energy (E_{em}), the oscillator strength (*f*), the main emission transition and the electric transition dipole moments, are listed in Table 2, and the simulated emission spectra of 1.7–2.6 eV are shown in Fig. 4. From Fig. 4, strong yellow emission in the region of 2.0–2.3 eV indicate three types of vacancy defects or impurities. The first type is the C_{Ga} impurity effect on the emission band of about 2.0 eV. The second is that V_{Ga}, V_N–H, Si_{Ga} and O_N arouse the yellow emission band of about 2.1 eV, which has been mentioned in a few literature [6, 13, 14]. The third type is in agreement with other literature [16–19]. It is the V_{Ga}–O_N complex that excites the yellow band around 2.2 eV. On the other hand, V_{Ga}–H:GaN, V_N:GaN, C_N:GaN and C_i:GaN clusters have no distinct emission band in yellow region. It

Table 2 Vertical emission excitation energy, oscillator strength, main emission transition and electric transition dipole moments

	$E_{em.}$ (eV)	*f*	Main transition[a]	Electric transition dipole moments (Au)		
				x	*y*	*z*
GaN	2.15	0.0010	155B[Ga4s4p N2p] → 135B[N2p Ga4p] (88%)	−0.0051	0.0351	0.1351
V_{Ga}:GaN	2.11	0.0187	155B[N2p] → 145B[Ga4p N2p] (65%)	−0.4925	0.3158	0.1390
V_{Ga}-O_N:GaN	2.23	0.0227	155B[N2p Ga4p] → 143B[N2p Ga4p] (64%)	0.5369	0.3330	−0.1268
V_{Ga}-H:GaN	2.26	0.0068	154B[Ga4p N2p] → 127B[Ga4p] (75%)	−0.1036	−0.2456	−0.2294
V_N:GaN	–	–	–	–	–	–
V_N-H:GaN	2.11	0.0279	160A[N2s Ga4p] → 152A[Ga4s N2s] (81%)	0.0321	−0.6154	0.3972
C_{Ga}:GaN	2.01	0.0144	160A[N2s Ga4p C2p] → 150A[C2s N2p] (61%)	−0.0050	0.5418	−0.0182
C_N:GaN	2.22	0.0021	155B[N2p] → 136B[N2p] (93%)	0.0058	0.0085	0.1935
C_i:GaN	2.21	0.0005	161A[C2p N2p] → 156A[Ga4p] (73%)	0.0592	−0.0739	0.0201
Si_{Ga}:GaN	2.11	0.0328	169A[N2s Si3p Ga4p] → 161A[N2s Ga4s Si3s] (95%)	0.0236	−0.2559	−0.7366
O_N:GaN	2.06	0.0452	161A [N2s Ga4p] → 156A[N2s Ga4s4p] (93%)	0.0657	−0.3696	−0.8580

[a] Main components of MOs are in the square brackets and the percent contribution of transition is in the parenthesis

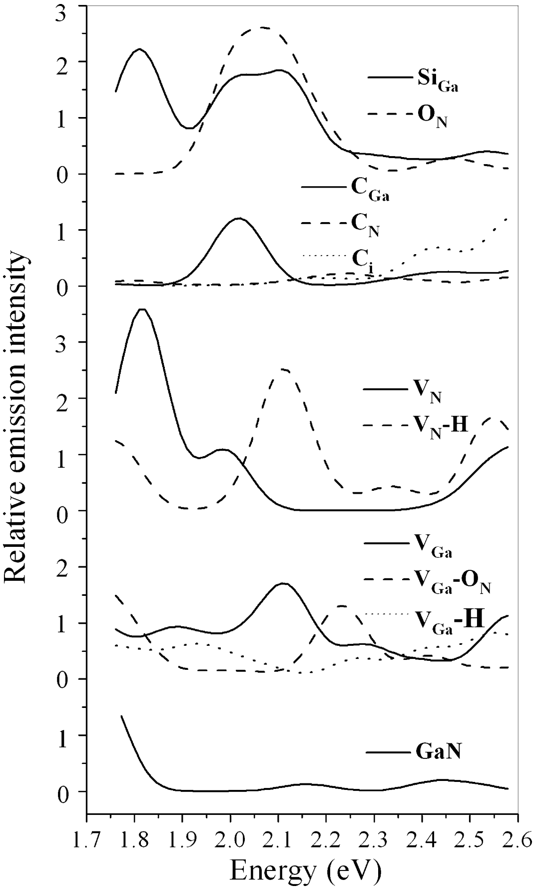


Fig. 4 Emission spectra of GaN clusters calculated by the TDDFT method

is well known that the oscillator strength that relates to the transition intensity is in direct ratio of the square of the transition dipole moments $|\langle A|P|B\rangle|^2$ [27], namely

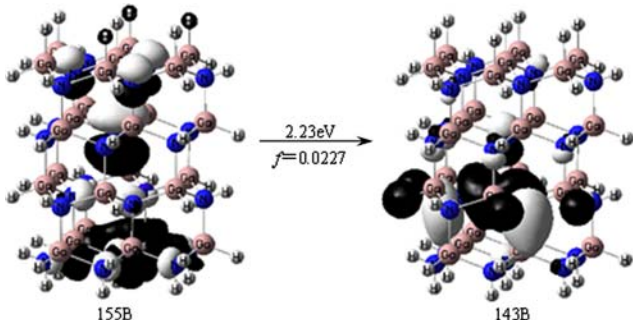


Fig. 5 Charge density maps of the transition MOs corresponding to the yellow emission band of the V_{Ga}–O_N:GaN cluster

$$f^{ed} = \frac{n(n^2+1)^2}{9}\frac{8\pi^2 mc}{3he^2\lambda}|\langle A|P|B\rangle|^2$$

where, f^{ed} is the oscillator strength, and P is the electric dipole moment operator. Figure 5 displays the charge density maps of the transition MOs corresponding to the yellow emission band of V_{Ga}–O_N:GaN cluster. If the center of the positive or the negative electric charge in the final state is apart from that in the initial state, the electric transition dipole moments $|\langle A|P|B\rangle|$ (Table 2) will increase, and then the intensity of the emission band becomes stronger. As the electric transition dipole moment in *x, y* and *z* direction is large (0.5369, 0.3330 and −0.1268), the yellow emission transition of V_{Ga}–O_N:GaN cluster is strong.

4 Conclusion

In summary, V_{Ga}–H, V_N, V_N–H, C_{Ga} or Si_{Ga} may have an effect on the absorption efficiency of GaN material from the excitation light of about 3.7 eV, because the absorption band of GaN cluster with these vacancy defects or impurities is strong. The yellow emission cases of these considered clusters divide into four types. The first type is the C_{Ga} impurity effect on the emission band of about 2.0 eV. According to the second, V_{Ga}, V_N–H, Si_{Ga} and O_N arouse the yellow emission band of about 2.1 eV. According to the third, it is the V_{Ga}–O_N complex that excites the yellow band of about 2.2 eV. Lastly, V_{Ga}–H:GaN, V_N:GaN, C_N:GaN and C_i:GaN clusters have no distinct emission band in yellow region.

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References

1. Denis A, Goglio G, Demazeau G (2006) Mater Sci Eng Rep 50:167. doi:10.1016/j.mser.2005.11.001
2. Nyk M, Jabłoński JM, Strek W, Misiewicz J (2004) Opt Mater 26:133. doi:10.1016/j.optmat.2003.11.011
3. Ogino T, Aoki M (1980) Jpn J Appl Phys 19:2395. doi:10.1143/JJAP.19.2395
4. Neugebauer J, Van de Walle CG (1996) Appl Phys Lett 69:503. doi:10.1063/1.117767
5. Korotkov RY, Reshchikov MA, Wessels BW (2003) Phys B 325:1
6. You W, Zhang XD, Zhang LM et al (2008) Phys B 403:2666. doi:10.1016/j.physb.2008.01.033
7. Suski T, Perlin P, Teisseyre H et al (1995) Appl Phys Lett 67:2188. doi:10.1063/1.115098
8. Van de Walle CG (1997) Phys Rev B 56:R10020. doi:10.1103/PhysRevB.56.R10020
9. Zhang R, Kuech TF (1998) Appl Phys Lett 72:1611. doi:10.1063/1.121144
10. Armitage R, William H, Yang Q et al (2003) Appl Phys Lett 82:3457. doi:10.1063/1.1578169
11. Kuriyama K, Mizuki Y, Sano H et al (2005) Solid State Commun 135:99. doi:10.1016/j.ssc.2005.03.051
12. Yang HC, Lin TY, Huang MY, Chen YF (1999) J Appl Phys 86:6124. doi:10.1063/1.371662
13. Kobayashi H, Gibson WM (1998) Appl Phys Lett 73:1406. doi:10.1063/1.121958
14. Laukkanen P, Lehkonen S, Uusimaa P et al (2002) J Appl Phys 92:786. doi:10.1063/1.1488241
15. Zhang XD, Lin DX, Li GP et al (2006) Acta Phys Sin 55(10):5487
16. Elsner J, Jones R, Heggie MI et al (1998) Phys Rev B 58:12571. doi:10.1103/PhysRevB.58.12571
17. Reshchikov MA, Morkoç H (2005) J Appl Phys 97:061301. doi:10.1063/1.1868059
18. Reshchikov MA, Morkoc H (2006) Phys B 376–377:428. doi:10.1016/j.physb.2005.12.110
19. Bouguerra M, Belkhir MA, Chateigner D et al (2008) Phys E 41:292. doi:10.1016/j.physe.2008.07.010
20. Halls MD, Schlegel HB (2001) Chem Mater 13:2632. doi:10.1021/cm010121d
21. Jacquemin D, Perpète EA, Scalmani G et al (2006) Chem Phys Lett 421:272. doi:10.1016/j.cplett.2006.01.068
22. Hu XL, Li JQ, Zhang YF et al (2009) Chem Phys Lett 468:83. doi:10.1016/j.cplett.2008.11.049
23. Hu XL, Li JQ, Zhang YF et al (2009) J Mol Struct THEOCHEM 900:27. doi:10.1016/j.theochem.2008.12.016
24. Jacquemin D, Perpète EA, Scuseria GE et al (2008) J Chem Theory Comput 4:123. doi:10.1021/ct700187z
25. Brena B, Ojamäe L (2008) J Phys Chem C 112:13516. doi:10.1021/jp8048179
26. Tomić S, Montanari B, Harrison NM (2008) Phys E 40(6):2125. doi:10.1016/j.physe.2007.10.022
27. Powell RC (1997) Physics of solid-state laser materials. Springer, Berlin