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Effects of dopant concentration on structural and near-infrared luminescence of Nd^{3+}-doped beta-Ga_2O_3 thin films

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We have investigated structural and near-infrared (NIR) luminescence of Nd^{3+}-doped β-Ga_2O_3 thin films (Nd:Ga_2O_3) with different Nd^{3+} doping concentrations. With an increase of Nd^{3+} content, the crystal lattice of the films expands, while the energy band gap shrinks. Moreover, NIR luminescence is investigated as a function of Nd^{3+} doping concentration. The measured results are related to the structural change and energy transfer of cross relaxation process ascribed to $^4F_{3/2}$—$^4I_{9/2}$, $^4F_{3/2}$—$^4I_{11/2}$, and $^4F_{3/2}$—$^4I_{13/2}$ of the phosphor films. This work implies that the enhanced NIR luminescence and blue-shift observation are associated with the lattice distortion and the variation in the crystal field of Nd: Ga_2O_3. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4919586]

Lanthanide-doped semiconductors have attracted continuous attentions for their potential applications in optoelectronic devices such as optical imaging devices, waveguides, and amplifiers.[1–7] It is well-known that the luminescence efficiency of dopant emissions could be highly improved with a wide bandgap host.[8] Moreover, the wide bandgap semiconductors exhibit highly thermal and chemical stability, which make them ideal hosts for lanthanide ions. As one of wide bandgap semiconductors (~4.9 eV), β-Ga_2O_3 has been proved to serve as a desirable material in many fields such as solar-blind photodetector, gas sensor, electron-luminescent device, transparent conducting oxide, and field-effect transistor.[9–12] β-Ga_2O_3 also behaves as an n-type semiconductor due to the presence of a donor band related to intrinsic oxygen deficiency.[13] Many groups have reported the effect on the structural and luminescence properties of some lanthanide ions doped Ga_2O_3.[14–17] Among these dopants, particular interests have been shown on neodymium (Nd) with near-infrared (NIR) emission at ~1100 nm corresponding to $^4F_{3/2}$–$^4I_{11/2}$ transition, which is widely used for high power laser media with a high stimulated emission cross-section.[18,19] The related physical properties of Nd dopant have been examined in many semiconductor matrices such as TiO_2, GaN, and AlN phosphors.[20–22] However, previous studies have seldom focused on the incorporation of Nd ion into Ga_2O_3. There are many fundamental properties of Nd:Ga_2O_3 that remain insufficiently unknown or evaluated. On the other hand, compared to powders, luminescent thin films provide several advantages, such as higher thermal stability, better adhesion to the solid surface, higher lateral resolution from smaller grains, and reduced outgassing rate, which makes them prominent applications in flat-panel displays, light sources, and integrated optics systems.[7] Therefore, further systematic study of the structural and luminescence properties of Nd:Ga_2O_3 film is of vital importance for the future applications. In this work, we present the results of investigating Nd doped β-Ga_2O_3 thin films with various dopant concentrations. The correlation between the optical properties and lattice distortions is studied. Spectroscopic evidence is provided for the doping of Nd ion into the β-Ga_2O_3 lattice. The crystal field analysis for the observed enhancement in NIR luminescence and blue-shift is carried out.

Nd-doped β-Ga_2O_3 films with the thickness of 200 nm were deposited on (0001) Al_2O_3 substrates with the dimension of 10 mm × 10 mm × 0.5 mm by radio frequency magnetron sputtering. A Ga_2O_3 disk embedded by several strips of Nd_2O_3 was used as the target. The Nd concentrations were controlled by solely changing the strips numbers during the deposition. The Nd concentrations in Nd: Ga_2O_3 films were determined as 0.4 mol. %, 0.8 mol. %, 1.2 mol. %, and 1.6 mol. % by the X-ray energy dispersive spectroscopy (EDS). The base pressure in the sputtering chamber was 1×10^{-4} Pa. The growth temperature and Ar gas pressure were fixed at 750 °C and 1 Pa, respectively. The power applied to the Nd:Ga_2O_3 target was set at ~80 W. The crystal structure was measured by a Bruker D8 Advance X-ray diffractometer (XRD). Ultraviolet-visible (UV-vis) absorption spectrum was taken using a Hitachi U-3900 UV-visible spectrophotometer. The valences of Nd ions were analyzed by X-ray photoelectron spectroscopy (XPS). The photoluminescence (PL) spectra were recorded using an Edinburgh FLSP920 spectrophotometer equipped with a He-Cd laser

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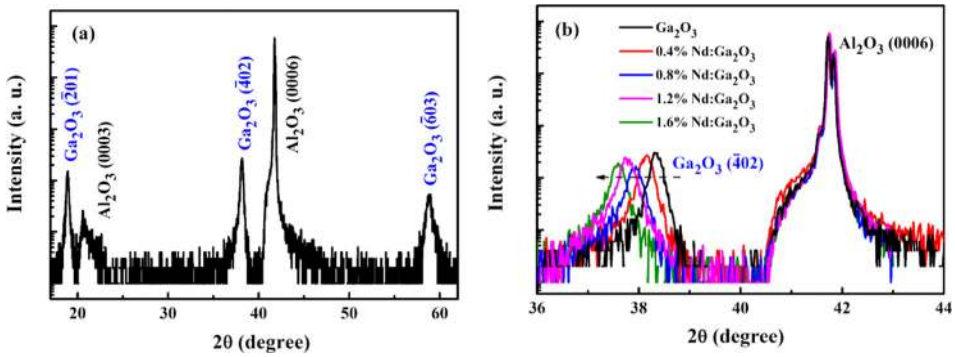

FIG. 1. (a) XRD patterns of the β-Ga_2O_3. (b) θ-2θ spectrum in a narrow range of the Nd:Ga_2O_3 films with different doping concentration level (0%, 0.4%, 0.8%, 1.2%, and 1.6%).

(325 nm). And the laser beam with a power of 30 mW was focused on the center of the Nd:Ga_2O_3 sample. NIR PL spectra were detected with a nitrogen-cooled NIR photomultiplier tube (Hamamatsu C9940–02). All the measurements were carried out at room temperature.

The crystallinity and crystallographic orientation of the formed Nd:Ga_2O_3 films were examined by XRD. Fig. 1(a) shows the θ–2θ spectrum of the 200 nm thick undoped β-Ga_2O_3 film deposited on (0001) sapphire single-crystal substrate. Only the ($\bar{2}$01) peak of β-Ga_2O_3 is presented along with that of the Al_2O_3 substrate. This result indicates that the β-Ga_2O_3 thin film is grown with its ($\bar{2}$01) plane normal to the Al_2O_3 substrate. Fig. 1(b) demonstrates the XRD patterns in a small angle range around the Nd:Ga_2O_3: ($\bar{4}$02) reflection peaks with various amounts of Nd-doping level (0%, 0.4%, 0.8%, 1.2%, and 1.6%). As clearly seen from the XRD patterns, the Nd doping can induce remarkable modification in the structural properties of the films. The peak position of the Nd:Ga_2O_3 ($\bar{4}$02) peaks shift to lower angles with an increase of Nd dopant concentration. It is known that monoclinic β-Ga_2O_3 lattice has two distinct crystallographic sites, where Nd ions can substitute either a highly distorted octahedral site (O_h point symmetry) or a slightly distorted tetrahedral site (T_d point symmetry). Taking into account, the magnitudes of the ionic radii (Nd^{3+}: 0.983 Å, Ga^{3+} in octahedral coordination: 0.62 Å, Ga^{3+} in tetrahedral coordination: 0.47 Å), the most probable site for the Nd ions substitution is at the octahedral sites of the β-Ga_2O_3 lattice. Similar results were also drawn in Dy:Ga_2O_3, Er:Ga_2O_3, and Eu:Ga_2O_3.[14,15,17,23] Due to the large difference of the ionic radii between the dopant ions and the Ga ions of host, the strong lattice expansion along the ($\bar{2}$01) lattice plane indicates that Nd^{3+} ions enter the Ga_2O_3 lattice substitutionally. Note that neither peaks corresponding to Nd_2O_3 nor other Nd-related phases are found in the XRD patterns, confirming that Nd^{3+} ions are well incorporated into the Ga^{3+} site. The shifts in the 2θ values corresponding to the ($\bar{2}$01) plane distance of Nd:Ga_2O_3 lattice are well reflected in the variation of the lattice distortion with the Nd^{3+} concentration. When the Nd concentration increases, the lattice distortion is gradually enhanced. The full-width at half-maximum (FWHM) of the Nd:Ga_2O_3 ($\bar{4}$02) peak was used to evaluate the dependence of crystalline quality. By employing Scherrer's formula, the average size of the crystal grains can be estimated. It is found that higher lattice distortion results in larger crystalline size, which reveals the degradation of the crystallinity of the films.

The optical absorption of the Nd:Ga_2O_3 films was characterized by UV-vis absorbance measurements to confirm the band gap energy of the samples. Fig. 2(a) shows the absorbance spectra of Nd:Ga_2O_3 film along with pure β-Ga_2O_3 film. The spectra of the host exhibit a sharp intrinsic absorption edge at the wavelength of around 250 nm, whilst those of Nd-doped samples display obvious red-shift.[8] The band gap is fitted by extrapolating the linear region of the plot $(\alpha h\nu)^2$ versus $h\nu$, as shown in the inset of Fig. 2(a). The bandgap decreases from 4.93 eV for pure β-Ga_2O_3 to 4.61 eV for 1.6% Nd:Ga_2O_3 film. Such reduction of the band gap could be attributed to new unoccupied electron states in the gap below the conduction band edge due to the location of Nd ions on the substitutional sites of Ga_2O_3. In fact, the observed red-shift in the band gap was found to correlate with the lattice distortions reflected in the d spacing of ($\bar{2}$01) plane well, as shown in Fig. 2(b). A larger d spacing is expected to result in a narrow band gap, which is similar to the band gap variation reported by other groups.[20,24,25]

The deposited Nd:Ga_2O_3 (1.2%) films were characterized using XPS to illustrate the chemical compositions and chemical states of oxide films.[26,27] The charge-shift spectrum was calibrated using the fortuitous C 1 s peak at 284.8 eV. It is noted that two symmetrical peaks of Ga $2p_{1/2}$ and Ga $2p_{3/2}$ were located at 1145.5 eV and 1118.5 eV, respectively (Fig. 3(a)). The separation distance between these two peaks is about 27 eV, which is in good agreement with the binding energy of the Ga 2 p ($\Delta = 26.8$ eV).[28] Fig. 3(b) reveals the high resolution XPS spectra of Nd $3d_3$ and Nd $3d_5$ peaks, centered at 1005.7 eV and 982.9 eV, respectively. Our measured values are slightly smaller than the standard data for Nd $3d_3$ and Nd $3d_5$, suggesting a potential host effect from Ga_2O_3 on the chemical environment of Nd. Therefore, XPS results confirmed that Nd atoms have been effectively incorporated into the oxide matrix and participate in the chemical bonding. The O 1 s peak is split into two peaks, as shown in Fig. 3(c). The main peak at 530.8 eV could be assigned to the oxygen in Ga_2O_3 lattice, while the peak at 532.1 eV could be due to the C/O bonds related to carbonaceous contamination.[29] The compositional ratio of Ga-to-O is about 1:1.43, which is close to the stoichiometric ratio (Ga_2O_3: Ga-to-O = 1:1.5), indicating the presence of oxygen vacancies in the films.

Fig. 4(a) shows the NIR PL spectra of Nd:Ga_2O_3 thin films with different doping concentrations measured at room temperature. Compared to undoped β-Ga_2O_3 film, the pronounced NIR PL emission consists of three bands, corresponding to the infra-4f transitions of Nd^{3+} ions from $^4F_{3/2}$ level to

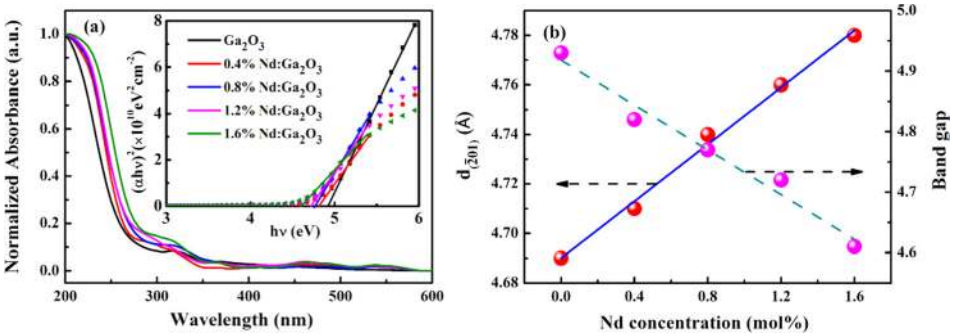

FIG. 2. (a) Absorption spectra of Nd:Ga_2O_3 thin films compared with that of undoped β-Ga_2O_3 thin film and the plot of $(\alpha h\nu)^2$ versus $h\nu$ in the inset. (b) Nd doping concentration dependence of $(\bar{2}01)$ lattice plane distance and the band gap, respectively.

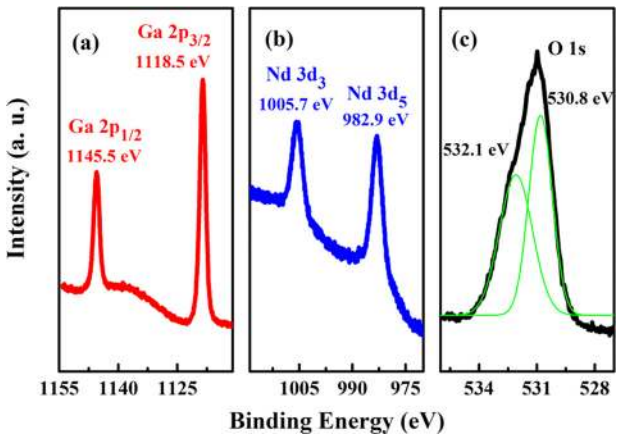

FIG. 3. XPS spectra of Ga 2p (a), Nd 3d (b), and O 1s (c) core level for Nd:Ga_2O_3 (1.2%) thin film.

$^4I_{9/2}$ (~905 nm), $^4I_{11/2}$ (~1067 nm), and $^4I_{13/2}$ (~1339 nm) levels, respectively. As seen, the emission intensity can be remarkably enhanced with increasing Nd^{3+} doping concentration in the Nd:Ga_2O_3 films. An enhancement factor of main $^4F_{3/2}$–$^4I_{11/2}$ transition band can reach up to 2.3. As discussed above, the distorted octahedral site with an inversion center should be more suitable to accommodate Nd ions, presenting the selection rules forbidding all 4f–4f electric dipole (ED) transitions. With Nd dopant concentration increases, the c-axis of the lattice elongates (Fig. 2(b)) and promotes the structure asymmetry of the Ga_2O_3 host, approaching lower symmetry around Nd^{3+} ions. In principle, the lower symmetry on the site of Nd ions means that the more uneven crystal-field components can mix opposite-parity into 4f configurational levels and subsequently increase the ED transition probabilities of the dopant ions. Herein, the increase in the ED transition probabilities relating to the elongation of d spacing of $(\bar{2}01)$ plane should be responsible for the enhancement of NIR PL emission. Note that no corresponding excitation peaks related to Nd^{3+} ions were seen in the UV-Vis absorption spectra. Thus, the direct UV excitation of Nd^{3+} ions in Nd:Ga_2O_3 can be negligible.[19,20] The above-mentioned results demonstrate the existence of efficient energy transfer (ET) from the electron-hole pairs created in the Ga_2O_3 host to Nd^{3+} ions. In this process, the Ga_2O_3 will act as an effective light harvest to absorb UV photons and subsequently transfer energy to Nd^{3+} ions and thereby resulting in the typical luminescence of the Nd^{3+} ions. Similar observations have been reported in Nd:$SrTiO_3$, Nd:TiO_2, etc.[19,30] In our study, the excitation energy of incident light is lower than the band gap of Nd:Ga_2O_3. Owing to the existence of oxygen vacancy defects in the films, hence, the ET process between the Ga_2O_3 host and Nd ion might be as follows. Through ground state absorption (GSA) process, the electrons are excited from the valence band to the donor band (oxygen vacancy) by the light source. The released energy due to the recombination of electrons in the defect state with the photogenerated holes can transfer to the excited states of the Nd ions; thereby, NIR emissions of Nd take place. Notably, the NIR emission bands from Nd: Ga_2O_3 thin films present an obvious blue-shift, the main luminescent peak ($^4F_{3/2}$—$^4I_{11/2}$) shifts from 1077 nm to 1065 nm (inset of Fig. 4(a)). The observed phenomena can be explained by the variation in the crystal field around Nd^{3+} ions, caused by

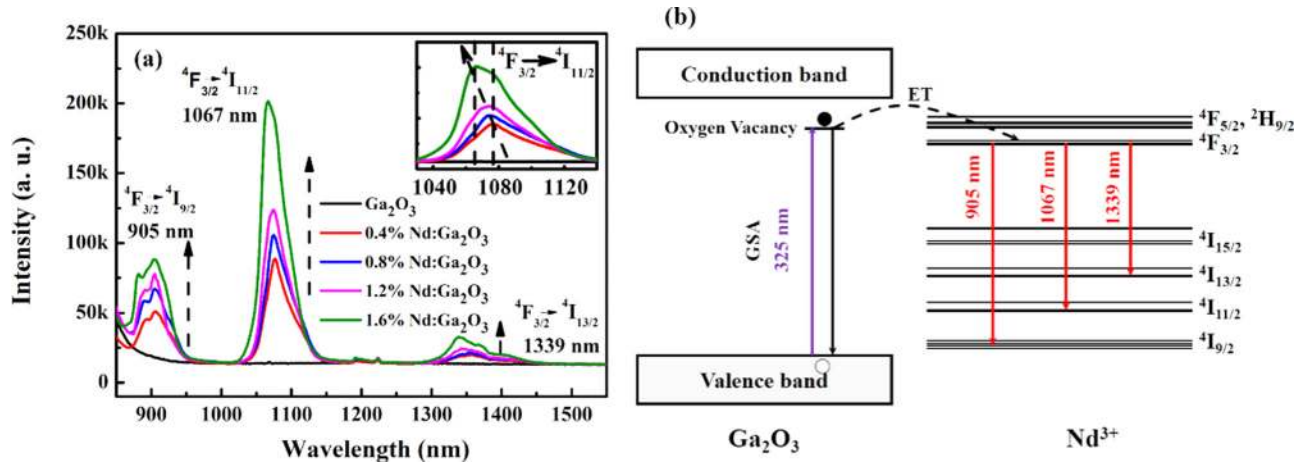

FIG. 4. (a) NIR PL spectra of Nd:Ga_2O_3 films with different doping concentrations. Inset shows the enlarged PL spectra around 1080 nm. (b) Energy level diagram of Ga_2O_3 and Nd^{3+}, as well as the proposed mechanisms less than 325 nm laser excitation.

lattice distortion. As discussed above, with increasing the Nd concentration, the lattice distortion is gradually enhanced. The increase of the octahedral distortion leads to the enhancement in the Stark splitting of the $^4F_{3/2}$ multiplet. Thus, the enhanced Stark emitting levels are splitted from the $^4F_{3/2}$ state, causing the blue-shift.[31]

In conclusion, monoclinic Nd:Ga_2O_3 thin films with a preferable ($\bar{2}01$) orientation were grown on α-Al_2O_3 (0001) substrates by radio frequency magnetron sputtering. The structural and optical spectroscopy of Nd:Ga_2O_3 thin films have been systematically investigated. The evolution of lattice expansion and optical spectra with increasing the doping concentration shows the chemical substitution of Nd^{3+} ions into the Ga_2O_3 crystal lattice. The lattice distortion and the variation in the crystal field play important roles in the observed peak intensity enhancement and wavelength blue-shifts of NIR luminescence. These results may provide a new insight for further various optoelectronics applications from Nd:Ga_2O_3 films.

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