



CrossMark  
 click for updates

Cite this: *RSC Adv.*, 2017, 7, 9160

# Structural, optical and magnetic properties of N ion implanted CeO<sub>2</sub> thin films

Pawan Kumar,<sup>a</sup> Parmod Kumar,<sup>b</sup> Ashish Kumar,<sup>b</sup> Indra Sulania,<sup>b</sup> F. Chand<sup>\*a</sup> and K. Asokan<sup>\*b</sup>

The present study reports the structural, morphological, optical and magnetic properties of N ion implanted CeO<sub>2</sub> thin films deposited by RF magnetron sputtering technique. These CeO<sub>2</sub> thin films were implanted with N ions having an energy of 80 keV with varying fluencies of  $1 \times 10^{15}$ ,  $1 \times 10^{16}$  and  $6 \times 10^{16}$  ions per cm<sup>2</sup>, respectively. X-ray diffraction measurements show that as deposited films had predominantly (111) orientations. There is a significant change in the crystalline nature of these films after implantation compared to pristine film. RBS measurements confirm the presence of N ions in CeO<sub>2</sub> thin film with the highest fluence. The closely packed circular shaped nanoparticles were observed through AFM images both in pristine and N ion implanted CeO<sub>2</sub> films and these were agglomerated on the surface at a fluence of  $6 \times 10^{16}$  ions per cm<sup>2</sup>. The crystalline structure and defect related information were evident through Raman spectroscopy. Raman results show that the crystalline structure is maintained even after implantation while the defect related peak is highest for the fluence value of  $1 \times 10^{15}$  ions per cm<sup>2</sup> and decreases thereafter. The magnetic measurements show enhanced ferromagnetic ordering in N ion implanted CeO<sub>2</sub> films compared to pristine film. The saturation magnetization is highest for the lowest fluence of N ions ( $1 \times 10^{15}$  ions per cm<sup>2</sup>) which decreases with ion fluences. This diverse defect nature of oxygen vacancies (V<sub>O</sub>) in the N ion implanted CeO<sub>2</sub> thin films mediates the ferromagnetic ordering.

Received 3rd July 2016

Accepted 23rd January 2017

DOI: 10.1039/c6ra17069b

rsc.li/rsc-advances

## 1. Introduction

CeO<sub>2</sub> is an important insulator that has been used in a wide variety of applications such as an epitaxial growth of buffer layers for high temperature superconducting thin films, high- $\kappa$  dielectric material in capacitors, solid oxide fuel cells, and as high oxygen storage devices.<sup>1,2</sup> This has also been extensively studied for efficient redox activities.<sup>3</sup> The discovery of room temperature ferromagnetism (RTFM) in various oxides doped with non-magnetic impurities has opened up a new direction in the field of spintronics. Due to the novel material properties and wide functionality, CeO<sub>2</sub> has been emerging as a superior oxide among the other rare earth oxides and as a potential candidate for spintronics applications.<sup>4,5</sup> The doping of transition metals like Mn, and Cu result in enhancement of ferromagnetism (FM) in CeO<sub>2</sub> nanocrystals.<sup>6,7</sup> The FM in diluted magnetic oxides (DMO) presents a major challenge in understanding its origin in such materials based on the general perception of exchange mechanisms. Dietl *et al.* proposed that the FM in DMO is not similar to the FM in group III–IV compounds like GaAs doped with Mn. The Zener model of the hole mediated mechanism is

one of the possible explanations to understand such FM interactions.<sup>8</sup> The exact origin behind FM in DMO is still a matter of discussion. However, the defects such as oxygen vacancies (V<sub>O</sub>), and the electronic configuration in lattice are known to play a major role in the FM.<sup>9</sup> Ge *et al.* proposed that the FM is strongly correlated in the presence of V<sub>O</sub>.<sup>10</sup> A report by Coey *et al.* suggested that the FM in DMO can be explained using F-center exchange mechanism which is based on trapping of electrons in V<sub>O</sub> (F-center) acting as coupling mediator between magnetic ions.<sup>11</sup> However, Liu *et al.* showed that the origin of RTFM in CeO<sub>2</sub> nanostructures is mediated by Ce vacancies rather than V<sub>O</sub>.<sup>12</sup> Ranjith *et al.* proposed that surface O defect states attribute exchange interaction between unpaired spins which ultimately governs the FM in CeO<sub>2</sub> nanoparticles.<sup>13</sup> Cruz *et al.* reported the magnetic properties of Ar and N ion implanted TiO<sub>2</sub> rutile single crystals wherein the observed FM has been associated with different types of defects.<sup>14</sup> Recently, RTFM has been reported in C ion implanted ZnO thin films.<sup>15</sup> In case of C ion doped ZnO, the experimental and theoretical calculations suggest that the substitution of O by C ions results in production of V<sub>O</sub> which results in ferromagnetic behaviour.<sup>16</sup> Elfimov *et al.* proposed that substitution of O with N ion leads to ferromagnetic behaviour in insulating oxides.<sup>17</sup> RTFM has also been observed in various non-TM doped metallic oxides such as Er doped ZnO, C-doped ZnO, and N-doped MgO.<sup>18–20</sup> Liu *et al.* reported spin polarized states as most stable when N ion

<sup>a</sup>Department of Physics, Kurukshetra University, Kurukshetra, Haryana-136119, India. E-mail: fchand@kuk.ac.in

<sup>b</sup>Materials Science Division, Inter University Accelerator Centre, New Delhi-110067, India. E-mail: asokaniuac@gmail.com



replaces O in MgO.<sup>21</sup> Kapilashrami *et al.* proposed that magnetization in N-doped MgO is strongly correlated with the formation of defects.<sup>22</sup> A report by Ben *et al.* suggested that FM in MgO nanosheets is attributable to unpaired electrons trapped at V<sub>O</sub>.<sup>23</sup> Ion implantation is an efficient technique for doping the small concentration of ions and it has been employed to introduce FM into metal oxides.<sup>24,25</sup> The dopant concentration can be precisely controlled in a selected area which is a unique advantage of this technique. However, a large numbers of defects are introduced in materials as a result of ion implantation. These defects will certainly influence the ferromagnetic properties of implanted samples. As N ion has an ionic radius comparable to O and it is most suitable dopant.<sup>26</sup> The substitution of N at O sites implies creation of different kinds of defects which are in turn responsible for significant modification in various physical properties. Even though there are many reports on the RTFM in CeO<sub>2</sub>, there are no reports about the effects of N ion implantation on the structural, optical, and magnetic properties. These magnetic films have potential applications in data storage devices, magnetic strips, actuators, magnetic sensors and microwave devices *etc.*<sup>27,28</sup>

Considering the importance of these materials, present study focuses on the detailed understanding of structural, morphological, optical and magnetic properties of N ion implanted CeO<sub>2</sub> thin films deposited by RF sputtering. This also provides an opportunity to understand the role of defects such as V<sub>O</sub> and to establish the RTFM in CeO<sub>2</sub> system.

## 2. Experimental details

CeO<sub>2</sub> thin films were deposited on Si (111) substrates using RF magnetron sputtering. Before deposition, these substrates were cleaned by acetone and trichloroethylene. The chamber vacuum was better than  $2 \times 10^{-5}$  torr which is normally required for depositing high quality films. The deposition was carried out in Ar gas environment at RF power of 150 W for 1 hour at room temperature (*i.e.* without substrate heating). These CeO<sub>2</sub> films were then implanted with 80 keV of N<sup>+</sup> ion beam with a beam current of 2  $\mu$ A using low energy ion beam facility (LEIBF) at Inter University Accelerator Centre (IUAC), New Delhi. The implantation was performed at three ion fluences;  $1 \times 10^{15}$ ,  $1 \times 10^{16}$  and  $6 \times 10^{16}$  ions per cm<sup>2</sup>. These N ion fluences correspond to the total at% of N ions in CeO<sub>2</sub> films  $\sim$ 0.14, 1.4 and 8.4 respectively. These were estimated using TRIM simulation and confirmed by RBS measurements and XRUMP simulation. Hereafter these films are referred as: P (pristine CeO<sub>2</sub> film), N<sub>1E15</sub> (CeO<sub>2</sub> N-ion implanted with fluence of  $1 \times 10^{15}$  ions per cm<sup>2</sup>), N<sub>1E16</sub> ( $1 \times 10^{16}$  ions per cm<sup>2</sup>) and N<sub>6E16</sub> ( $6 \times 10^{16}$  ions per cm<sup>2</sup>). X-ray diffraction measurements were performed using X-ray diffractometer (Bruker D8) with CuK $\alpha$  radiation ( $\lambda = 1.54$  Å) in order to obtain structural information within 20–60° range with step size of 0.02°. The Rutherford backscattering (RBS) measurements were performed with 2 MeV H<sup>+</sup> ions at IUAC, New Delhi. The incident and scattering angles were maintained at 7° and 170° respectively. The surface morphology of pristine and N ion implanted films was examined by a Multi Mode Scanning Probe Microscopy with Nanoscope IIIa controller

from Digital/Veeco Instruments Inc. in tapping mode using RTESP tip with a tip radius of  $\sim$ 10 nm. The Raman spectra were recorded by using Renishaw InVia Raman microscope using wavelength ( $\lambda = 514$  nm). The UV-VIS reflectance spectra were obtained using UV-vis Spectrophotometer (Model 2550). The photoluminescence (PL) spectra were carried out using the Spectrofluorometer (Shimadzu RF-5301PC). Furthermore, the magnetic properties were studied using vibrating sample magnetometer (VSM) (MicroSense EZ9 VSM).

## 3. Results and discussion

### 3.1 X-ray diffraction

To study the effect of N ion implantation on the structural parameters such as lattice parameter, strain and crystallite size in CeO<sub>2</sub> thin films, XRD measurements were carried out at room temperature. The XRD pattern of P and N ion implanted films are shown in Fig. 1. The sharp peaks are observed at the diffraction planes (111), (200), (220) and (311). These peaks match well with JCPDS card no. 75-0390 corresponding to the FCC fluorite structure of CeO<sub>2</sub> lattice. The intensity of prominent peak at 28.38° *i.e.*, (111) plane of N ion implanted films is significant and FWHM decreases with increasing ion fluences compared to the P film. The increasing intensity in XRD peak signifies an improvement in crystalline nature of CeO<sub>2</sub> films with N ion implantation. The average crystallite size of the CeO<sub>2</sub> is estimated from most prominent peak corresponding to (111) reflection plane using the Scherrer's formula<sup>29</sup> and listed in Table 1,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where  $D$  is the crystallite size,  $\lambda$  (1.54 Å) is wavelength of X-ray,  $\beta$  is FWHM and  $\theta$  is Bragg's diffraction angle. The calculated data is shown in Table 1. The dislocation density ' $\delta$ ' which is total length of dislocation lines per unit volume is measured

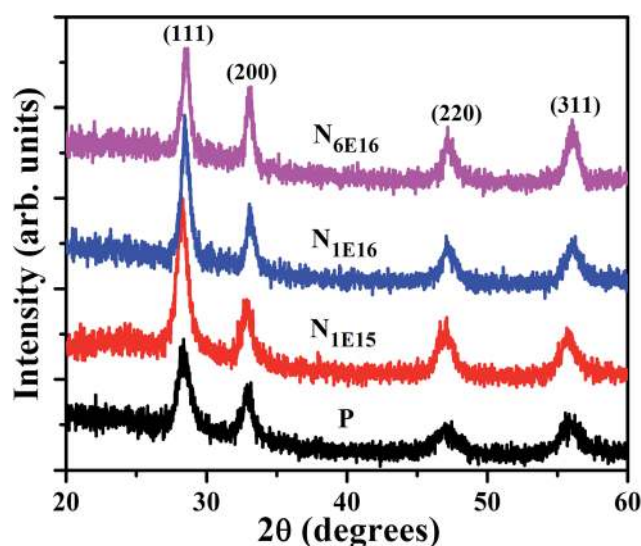


Fig. 1 XRD patterns of P and N ion implanted CeO<sub>2</sub> thin films.



**Table 1** Structural and morphological parameters of P and N ion implanted CeO<sub>2</sub> thin films. The crystallite size, lattice parameter, strain and dislocation density were obtained from XRD while roughness and particle size from AFM

Ion fluence (ions per cm <sup>2</sup> )	Crystallite size (nm)	Lattice parameter (Å)	Strain (ε) × 10 <sup>-2</sup>	Roughness (nm)	Dislocation density, δ × 10 <sup>12</sup> (m <sup>-2</sup> )	Particle size (nm)
P	8.0	5.441	7.11	3.20	1.547	59.4
N <sub>1E15</sub>	8.7	5.462	6.41	2.62	1.327	60.2
N <sub>1E16</sub>	10.8	5.421	6.34	2.61	0.853	61.3
N <sub>6E16</sub>	11.8	5.417	3.15	2.56	0.718	81.7

using  $\delta = 1/D^2$ .<sup>30</sup> The dislocation density is found to decrease with ion fluences as given in Table 1. This decrease in the dislocation density corresponds to reduction of the disorder with increasing N ion fluence inside CeO<sub>2</sub> films. Furthermore, the lattice parameter of CeO<sub>2</sub> thin films is measured using the following expression,<sup>31</sup>

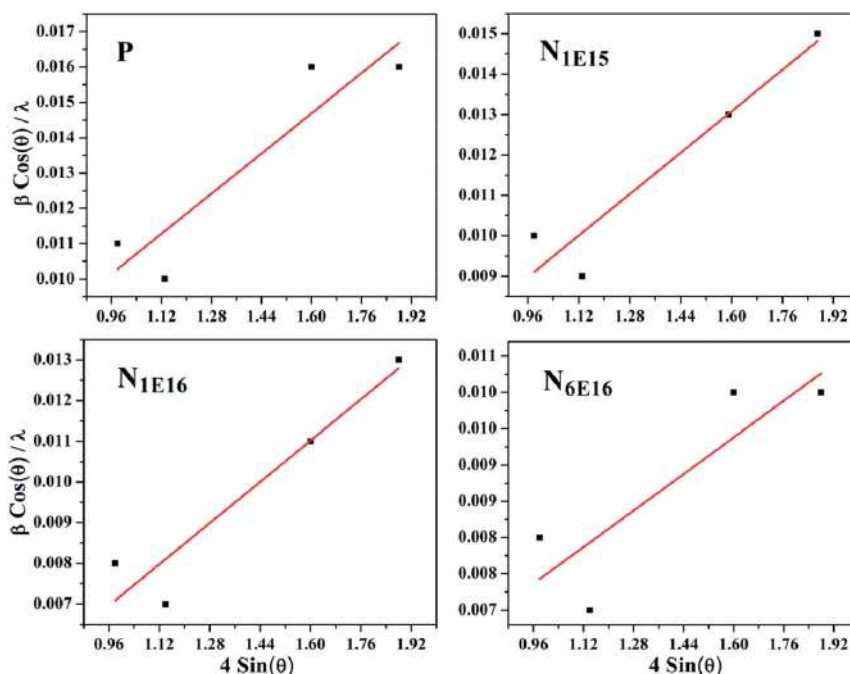
$$a^2 = \left[ \frac{\lambda^2}{4 \sin^2 \theta} \right] (h^2 + k^2 + l^2) \quad (2)$$

where  $a$  is lattice constant for FCC structure of CeO<sub>2</sub>. The lattice parameter of P film (5.441 Å) is found larger than the bulk CeO<sub>2</sub>, (5.411 Å) (JCPDS card no. 75-0390). It is also observed that lattice parameter of N<sub>1E15</sub> film is higher compared to N<sub>1E16</sub> and N<sub>6E16</sub> films. This suggests that at lower concentration of N ions, these are likely to occupy O sites. It may be noted that the ionic radius of N (1.71 Å) ion is slightly larger than that of O (1.40 Å). Hence, this is likely to change in lattice parameter and create lattice strain which in turn affects various physical properties of CeO<sub>2</sub> thin films. The strain 'ε' is estimated using Williamson–Hall (W–H) analysis,<sup>32</sup> as shown in Fig. 2. The graphs were plotted between  $4 \sin(\theta)$  (x-axis) and  $\beta \cos(\theta)/\lambda$  (y-axis). The slope of the linear fitted data corresponds to strain in the sample and listed

in Table 1. The strain is found to be maximum for the P film and reduces with N ion fluence in the films. This indicates strain relaxation in the films after N ion implantation. The positive value of strain 'ε' corresponds to tensile strain in CeO<sub>2</sub> thin films.

### 3.2 Rutherford backscattering (RBS) spectrometry

In order to confirm the composition and thickness of the deposited films, RBS measurement was performed and then simulated with XRUMP software (Fig. 3). The simulated spectra show that the average thickness of the films are ~300 to 320 nm and the Ce : O ratio is 1 : 2. It is evident from Fig. 3 that N is detected for the highest fluence film (N<sub>6E16</sub>). However, for lower fluences (N<sub>1E15</sub> and N<sub>1E16</sub>) implanted films, the signal from N in RBS was very weak because of low concentrations. Further, to confirm the depth and the distribution of N ions in CeO<sub>2</sub> thin films the TRIM calculations were carried out using SRIM software. From the Fig. 4, the depth of N ions in CeO<sub>2</sub> thin films is found to be ~110 nm and the distribution is Gaussian in nature. The observed depth of N ions inside CeO<sub>2</sub> thin film is consistent with the simulation of the RBS data using XRUMP software.



**Fig. 2** W–H plot of P and N ion implanted CeO<sub>2</sub> thin films.



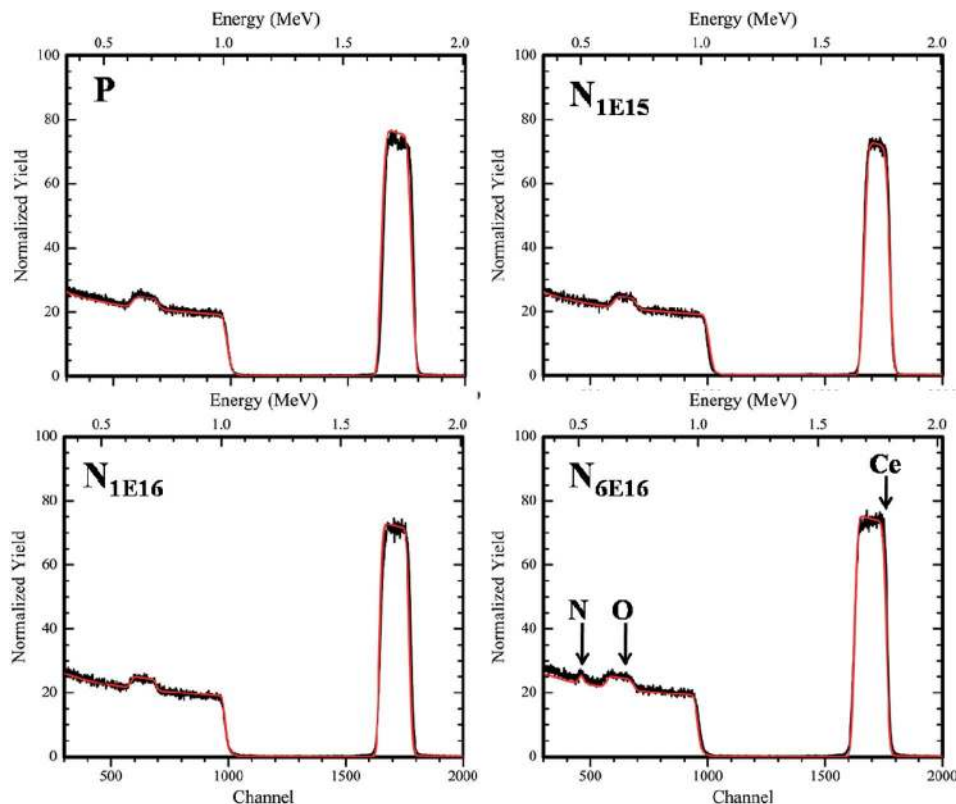


Fig. 3 Simulated RBS spectra of P and N ion implanted  $\text{CeO}_2$  thin films.

### 3.3 Atomic Force Microscopy (AFM)

Fig. 5 shows AFM images of P and N ion implanted  $\text{CeO}_2$  films. The formation of closely packed circular shaped nanoparticles on the surface of the films is clearly observed. It is evident that nanoparticles are well grown on the surface of the films and are uniformly distributed on  $2 \times 2 \mu\text{m}^2$  scan area of the films. However, the surface morphology of  $\text{N}_{6\text{E}16}$  is slightly different from the P,  $\text{N}_{1\text{E}15}$  and  $\text{N}_{1\text{E}16}$  films indicating the effect of higher energy deposition at higher fluence of N ions. The smaller

particles are agglomerated on the surface of  $\text{N}_{6\text{E}16}$  film. The average particle size and root mean square (RMS) surface roughness values of P,  $\text{N}_{1\text{E}15}$ ,  $\text{N}_{1\text{E}16}$  and  $\text{N}_{6\text{E}16}$  films are given in Table 1. It is observed that the surface roughness decreases with N ion implantation. The variation in particle sizes for P film and N ion implanted  $\text{CeO}_2$  thin films obtained from AFM are found to be consistent with the crystallite sizes of XRD (see in Table 1).

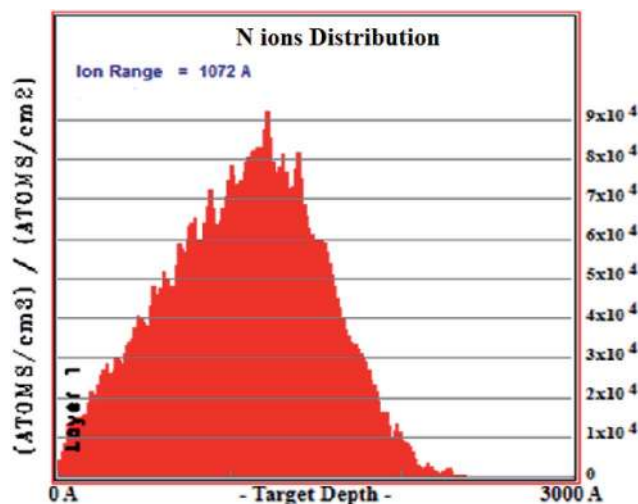


Fig. 4 Depth distribution of 80 keV N ions in  $\text{CeO}_2$  thin film.

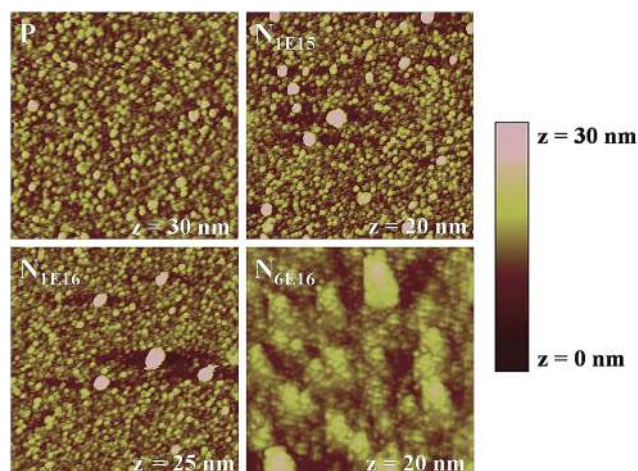


Fig. 5 AFM images (size:  $2 \times 2 \mu\text{m}^2$ ) of P and N ion implanted  $\text{CeO}_2$  thin films.



### 3.4 Raman spectroscopy

Raman spectroscopy provides the structural and additional details like defects created in the materials. Fig. 6 shows the Raman spectra of all the thin films investigated in this study. The prominent peak at  $\sim 443$  to  $463\text{ cm}^{-1}$  is ascribed to Raman-active vibrational mode ( $F_{2g}$ ) of  $\text{CeO}_2$ , which arises due to symmetrical stretching mode of O anions around Ce cations (O–Ce–O).<sup>33</sup> The Raman spectra of implanted films show small shift in  $F_{2g}$  mode towards higher wavelength and broadening in FWHM with ion fluence. Presence of inhomogeneous strain and defects contribute to the structural changes in the Raman spectra.<sup>34</sup> It is also evident that the intensity of  $F_{2g}$  mode enhances upto  $N_{1E16}$  ion fluence and the intensity decreases for  $N_{6E16}$  film. Besides, the prominent peak ( $F_{2g}$ ) mode in N ion implanted  $\text{CeO}_2$  thin films show additional peaks at about  $620\text{ cm}^{-1}$  and  $670\text{ cm}^{-1}$ . The peak positioned at  $\sim 620\text{ cm}^{-1}$  is attributed to intrinsic  $V_O$  that arise to the reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  ions. This indicates that O sublattice is affected as a result of change in grain size and doping.<sup>35</sup> However, the peak appears at around  $670\text{ cm}^{-1}$  might be attributed to second-order Raman transition of  $\text{CeO}_2$ .<sup>36</sup> Further, the intensity of intrinsic  $V_O$  mode at about  $620\text{ cm}^{-1}$  and second-order Raman transition about  $670\text{ cm}^{-1}$  in  $\text{CeO}_2$  films suppresses for higher N ion fluences (*i.e.*,  $N_{1E16}$  and  $N_{6E16}$ ).

### 3.5 UV-visible analysis

To determine the band gap energies of P and N ion implanted thin films, the Kubelka–Munk (KM) equation was employed which is given as,<sup>26</sup>

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} = F(R_\infty) \quad (3)$$

where  $K$ ,  $S$ ,  $R_\infty$  and  $F(R_\infty)$  are known as KM absorption coefficient, KM scattering coefficient,  $R_\infty = R_{\text{sample}}/R_{\text{standard}}$  and KM

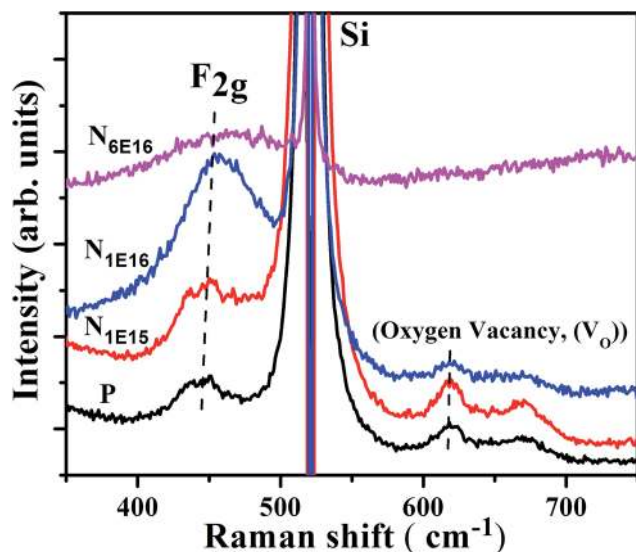


Fig. 6 Raman spectra of P and N ion implanted  $\text{CeO}_2$  thin films.

function respectively. The direct band gap of the semiconductor can be evaluated using the following equation,<sup>37</sup>

$$\alpha hv = C_1(hv - E_g) \quad (4)$$

where,  $\alpha$  is so called linear absorption coefficient of the material,  $C_1$  is a constant of proportionality and  $hv$  corresponds to photon energy. Using the KM function in eqn (4) following expression can be obtained,

$$[F(R_\infty)hv]^2 = C_2(hv - E_g)^{1/2} \quad (5)$$

Therefore, computing  $F(R_\infty)$  from eqn (3) and plotting  $[F(R_\infty)hv]^2$  vs.  $hv$ , the band gap ( $E_g$ ) of a films can be obtained.<sup>33</sup> Fig. 7 displays the UV-vis reflectance spectra of P film and  $N_{1E15}$ ,  $N_{1E16}$  and  $N_{6E16}$  thin films. The optical band gap of P film is found to be 3.22 eV which is consistent with literature.<sup>38</sup> It is observed that the band gap initially increases for  $N_{1E15}$  film (3.43 eV) and then it decreases for higher fluences  $N_{1E16}$  (3.22 eV) and  $N_{6E16}$  (2.98 eV). The variations in band gap for N ion implanted  $\text{CeO}_2$  are found to be consistent with XRD results. As discussed in XRD section, the N occupies interstitial site for  $N_{1E16}$  and  $N_{6E16}$  films compared with substitutional site for  $N_{1E15}$  film. Thus, the non-uniform distribution of N into  $\text{CeO}_2$  lattice for lower and higher fluences might be the reason behind the inconsistent change in band gap. This is also consistent with XRD and Raman data. It is believed that different kinds of defects are produced during N ion implantation. Similar results were reported by Xue *et al.* in optical band gaps after N ion implantation.<sup>39</sup>

### 3.6 Photoluminescence studies

The room-temperature PL spectra of the P and N ion implanted  $\text{CeO}_2$  thin films measured using 280 nm excitation wavelength are shown in Fig. 8. The PL spectra exhibit wide emission band  $\sim 395\text{ nm}$  ( $\sim 3.13\text{ eV}$ ) for P film and sharp emission bands for N ion implanted films  $\sim 370\text{ nm}$ . The strong UV emission for P and  $N_{1E15}$ ,  $N_{1E16}$  and  $N_{6E16}$  films indicate that optical band gap changes with N ion implantation. Based on this PL study, the emission bands lying between 365–400 nm for  $\text{CeO}_2$  thin films are ascribed to the charge transfer from Ce 4f to O 2p band due to different defect levels.<sup>40,41</sup> The weak bands at 400, 460 and 470 nm are found for N ion implanted films. The observed band gap results are consistent with UV-vis spectroscopic results. It is suggested that the strong emission  $\sim 369\text{ nm}$  for  $\text{CeO}_2$  is attributed to the defects like dislocations or O defects supporting for prompt O mobility.<sup>40,41</sup>

### 3.7 Magnetic measurements

Fig. 9 shows the magnetization ( $M$ ) vs. applied magnetic field ( $H$ ) dependence for P and N ion implanted  $\text{CeO}_2$  thin films. Inset in Fig. 9 displays the coercivity of P film and N ion implanted  $\text{CeO}_2$  thin films. It is evident that the values of saturation magnetization and coercivity are higher for N ion implanted films compared with P. Usually, pure  $\text{CeO}_2$  exhibits diamagnetic behaviour.<sup>42</sup> However, the presence of defects such as  $V_O$  charge imbalance and the nanosized effects are possible



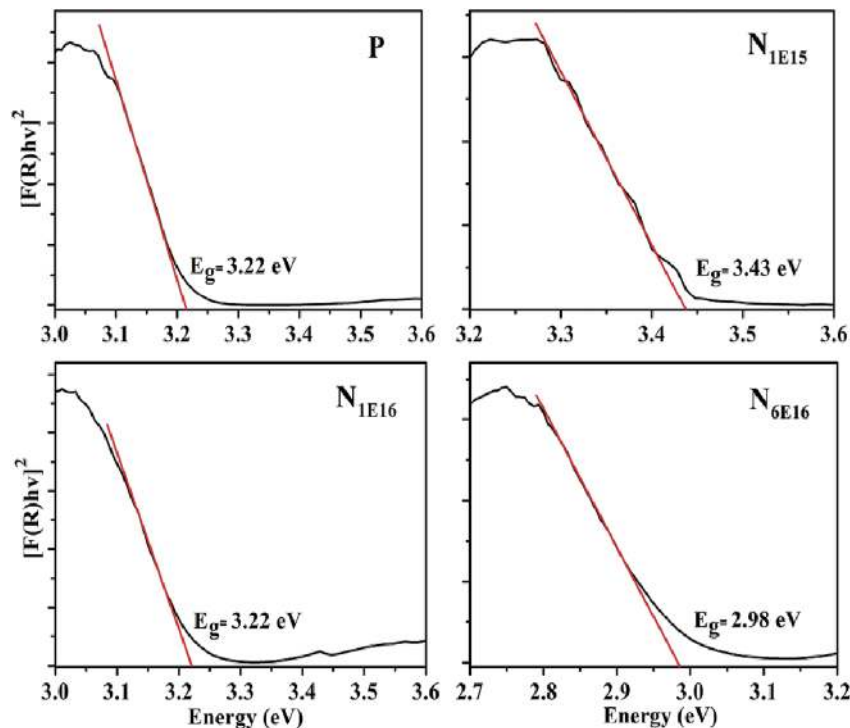


Fig. 7 UV-vis reflectance of P and N ion implanted  $\text{CeO}_2$  thin films.

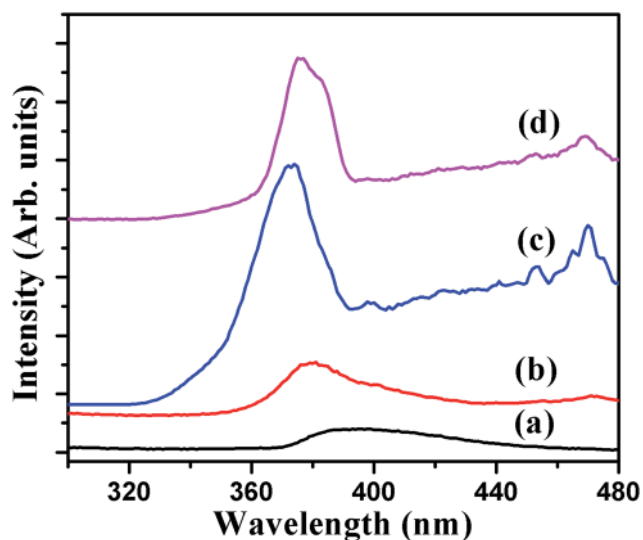


Fig. 8 Room-temperature PL spectra of P and N ion implanted  $\text{CeO}_2$  thin films: (a) P, (b)  $\text{N}_{1\text{E}15}$ , (c)  $\text{N}_{1\text{E}16}$ , and (d)  $\text{N}_{6\text{E}16}$ .

causes for FM in  $\text{CeO}_2$ .<sup>43</sup> It was proposed by Novica *et al.* that surface of nanoparticles plays a crucial role in RTFM which is an intrinsic property of nanocrystalline  $\text{CeO}_2$ .<sup>42</sup> The experimental and theoretical reports suggest that  $\text{V}_\text{O}$  plays an important role in establishing FM in nanosized  $\text{CeO}_2$  and there exist a strong correlation between  $\text{V}_\text{O}$  and the saturation magnetization.<sup>44,45</sup> Ge *et al.* proposed that spin polarization of 4f-shell electrons of Ce ions around  $\text{V}_\text{O}$  cause net magnetic moment for pure  $\text{CeO}_2$ .<sup>45</sup> It is accepted that the F-center exchange mechanism is suitable

to explain the ferromagnetic ordering in nanosized  $\text{CeO}_2$ .<sup>46</sup> In accordance to this,  $\text{V}_\text{O}$  (F-center) traps an electron which acts as a coupling agent between magnetic  $\text{Ce}^{3+}$  ions resulting in the formation of overlapped magnetic polarons. There are three possible charge states for the  $\text{V}_\text{O}$ : (a) when no electron is trapped in  $\text{V}_\text{O}$ , called  $\text{F}^{2+}$  center, (b) when one electron is trapped in  $\text{V}_\text{O}$  which can mediate ferromagnetic ordering known as  $\text{F}^+$  center, and (c) when two electrons are trapped in  $\text{V}_\text{O}$  and show singlet ( $S = 0$ ) state which mediates weak antiferromagnetic ordering known as  $\text{F}^0$  center.<sup>47,48</sup> It is predicted from theoretical

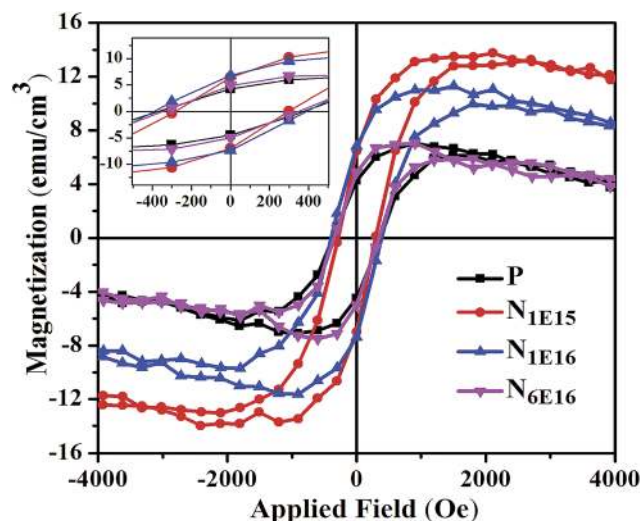


Fig. 9 Room temperature  $M - H$  plot of P film and N ion implanted  $\text{CeO}_2$  thin films.



calculation that  $V_O$  moves from nanoparticles interior to surface.<sup>49</sup> Previous reports suggest that surface layers play a significant role in the establishment of FM compared with interior of sample.<sup>50</sup> The substitution of N impurities near the vacancies may lead to form defect complexes which strongly affect the RTFM in MgO samples.<sup>24</sup> It is clearly seen from the Fig. 9 that P and N ion implanted films show hysteresis loops which indicate RTFM in CeO<sub>2</sub> films. The observed RTFM for pristine CeO<sub>2</sub> film might be recognized due to the presence of  $V_O$ . It is established from the XRD results that N occupies the O site in the host CeO<sub>2</sub> lattice. The inclusion of trivalent N ion at divalent O site generates excess charges which are compensated through the introduction of  $V_O$ . Therefore, the incorporation of N ion ( $N_{1E15}$ ) into the host CeO<sub>2</sub> lattice gives rise to increase in saturation magnetization up to a particular N concentration. This increase in  $V_O$  or O-related defects might be responsible for enhancement of saturation magnetisation in the  $N_{1E15}$  film. However, at higher fluence (*i.e.*  $N_{1E16}$  and  $N_{6E16}$ ), the N ions are distributed non-uniformly and occupy some interstitial sites as confirmed by XRD measurement. Incorporation of N ions at interstitial sites results in the suppression of magnetic moment and hence reduction in RTFM. The decrease in saturation magnetization with further increase in N ion fluence is correlated with decreasing  $V_O$ . The increasing  $V_O$  or defects at low fluence ( $N_{1E15}$ ) and decreasing  $V_O$  with further increase in N ion fluence compared with P is clearly evident from the Raman spectra (see Fig. 6). These observed results are in well agreement with C implanted ZnO thin films.<sup>15</sup>

Based on density functional theory (DFT) calculations, Valentin *et al.* suggested that N doping in anatase TiO<sub>2</sub> reduces the energy required for the formation of  $V_O$  in bulk form.<sup>51</sup> It is easy to reduce the pure rutile TiO<sub>2</sub> than anatase TiO<sub>2</sub>. This phase also favours the presence of substitutional N.<sup>52</sup> Furthermore, it is reported that in case of rutile phase, the energy required for the formation of vacancy reduces from 4.3 to 1.0 eV whereas for substitution of O with N from 9.7 to 6.4 eV.<sup>51</sup> As 2p orbital of  $N^{2-}$  occupies one electron less than O, the binding energy of the 2p bonding electrons is lower compared with the O ion.<sup>14</sup> In this way, the one electron state of  $N^{2-}$  ion will have larger orbital radius as compared to an isolated ion. At a suitable N concentration, the corresponding orbitals of the nearest defects will overlap, giving rise to a narrow impurity band with one hole per N ion leading to magnetic moment. For the two holes in 2p orbitals of O or N ions have lowest configurations that exhibit spin triplet state corresponding to the existence of an associated magnetic moment.<sup>14</sup> The overlapping between the defect states and the formation of a defect band may result in magnetic clusters and hence lead to induce RTFM in N ion implanted CeO<sub>2</sub> thin films. The interstitial occurrence of N ions suppresses the magnetic moments which result in the reduction of RTFM. The effect of C dopant on the magnetic properties of ZnO thin films has been studied theoretically as well as experimentally.<sup>15</sup> Pan *et al.* proposed experimentally as well as based on theoretical calculations (DFT) that the saturation magnetization increases for low carbon concentrations (from 0 to 1 at%). However, it decreases when C concentration reaches about 5 at% in the sample.<sup>53</sup> Zhou *et al.* also investigated experimentally the

effect of C concentration (at%) over magnetization and showed that the saturation magnetization is highest at C concentration ~2 at% whereas it reduced with higher concentration of C.<sup>54</sup> It has been suggested that the non-uniform distribution of C atoms at higher concentrations may be the reason. Based on theoretical studies, Ye *et al.* reported that the increase in the C content results in decrease in the separation among C–C ions favouring dominance of antiferromagnetic in the host lattice over the FM nature at higher concentration.<sup>55</sup> Based on these results, it is interpreted that strength of the exchange coupling is directly correlated with the separation between the C–C atoms. On the basis of above findings, in the present case the N ions are distributed non-uniformly inside host CeO<sub>2</sub> lattice at higher N fluences ( $N_{1E16}$  and  $N_{6E16}$ ). This is consistent with the findings of Kumar *et al.*<sup>15</sup> We have also observed that the maximum saturation magnetization is achieved at lower N concentration *i.e.*, 0.14% and decreases for the higher N ion concentrations (1.4% and 8.4%). In context of these calculations and observed experimental results, it is realized that the distribution of N inside the host CeO<sub>2</sub> lattice plays a significant role to modify the magnetic properties. The modification in the magnetic properties by N ion implantation provides an evidence for creating DMO material based spintronics.

## 4. Conclusions

The structural, morphological, optical and magnetic properties of N implanted CeO<sub>2</sub> thin films were investigated. The XRD confirmed the FCC structure corresponding to CeO<sub>2</sub>, and the Raman results show the presence of defects such as oxygen vacancies in these thin films. The band gap of CeO<sub>2</sub> film was found to be ~3.22 eV which is consistent with previous reports. RBS measurement confirms the presence of N ions in the CeO<sub>2</sub> films. The RTFM was observed in the pristine CeO<sub>2</sub> and an enhancement in saturation magnetization and residual magnetization for low fluence N ion implanted CeO<sub>2</sub> thin film. These changes are attributed to the creation of  $V_O$  due to N replacing O in CeO<sub>2</sub> lattice. A possible mechanism, the F-center exchange mechanism, is discussed to understand the FM ordering in these films. It is proposed that the distribution of N ions inside the host CeO<sub>2</sub> lattice plays a significant role to modify the magnetic properties.

## Acknowledgements

One of the authors, Pawan Kumar, is thankful to the CSIR, New Delhi for providing the SRF fellowship. He also gratefully acknowledges the support and encouragement received from Inter University Accelerator Centre, New Delhi, India.

## References

- 1 P. Singh, K. M. K. Srivatsa and S. Das, *Adv. Mater. Lett.*, 2015, **6**, 371–376.
- 2 A. Thurber, K. M. Reddy, V. Shutthanandan, M. H. Engelhard, C. Wang, J. Hays and A. Punnoose, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 165206.



- 3 A. Sharma, M. Varshney, H. J. Shin, Y. J. Park, M. G. Kim, T. K. Ha, K. H. Chae and S. Gautam, *Phys. Chem. Chem. Phys.*, 2014, **16**, 19909.
- 4 M. Venkatesan, C. B. Fitzgerald and J. M. D. Coey, *Nature*, 2004, **430**, 630.
- 5 N. H. Hong, J. Sakai, N. Poirrot and V. Brize, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 132404.
- 6 M. I. B. Bernardi, A. Mesquita, F. Béron, K. R. Pirota, A. O. de Zevallos, A. C. Doriguettod and H. B. de Carvalho, *Phys. Chem. Chem. Phys.*, 2015, **17**, 3072–3080.
- 7 J. C. Bear, P. D. McNaughtner, P. Southern, P. O'Brien and C. W. Dunnill, *Crystals*, 2015, **5**, 312–326.
- 8 T. Dietl, H. Ohno, F. Matsukura, J. Cibert and D. Ferrand, *Science*, 2000, **287**, 1019–1022.
- 9 X. P. Han, J. Lee and H. I. Yoo, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 100403.
- 10 M. Y. Ge, H. Wang, E. Z. Liu, J. F. Liu, J. Z. Jiang, Y. K. Li, Z. A. Xu and H. Y. Li, *Appl. Phys. Lett.*, 2008, **93**, 062505.
- 11 J. M. D. Coey, A. P. Douvalis, C. B. Fitzgerald and M. Vankatesan, *Appl. Phys. Lett.*, 2004, **84**, 1332–1334.
- 12 Y. L. Liu, Z. Lockman, A. Aziz and J. MacManus-Driscoll, *J. Phys.: Condens. Matter*, 2008, **20**, 165201.
- 13 K. S. Ranjith, P. Saravanan, S. H. Chen, C. L. Dong, C. L. Chen, S. Y. Chen, K. Asokan and R. T. Rajendrakumar, *J. Phys. Chem. C*, 2014, **118**, 27039–27047.
- 14 M. M. Cruz, R. C. da Silva, N. Franco and M. Godinho, *J. Phys.: Condens. Matter*, 2009, **21**, 206002.
- 15 P. Kumar, H. Malik and K. Asokan, *EPL*, 2015, **110**, 67006.
- 16 H. Pan, J. B. Yi, L. Shen, R. Q. Wu, J. H. Yang, J. Y. Lin, Y. P. Feng, J. Ding, L. H. Van and J. H. Yin, *Phys. Rev. Lett.*, 2007, **99**, 127201.
- 17 I. S. Elfimov, A. Rusydi, S. I. Csiszar, Z. Hu, H. H. Hsieh, H. J. Lin, C. T. Chen, R. Liang and G. A. Sawatzky, *Phys. Rev. Lett.*, 2007, **98**, 137202.
- 18 P. Kumar, V. Sharma, A. Sarwa, A. Kumar, S. Surbhi, R. Goyal, K. Sachdev, S. Annapoorni, K. Asokan and D. Kanjilal, *RSC Adv.*, 2016, **6**, 89242.
- 19 H. Pan, J. B. Yi, L. Shen, R. Q. Wu, J. H. Yang, J. Y. Lin, Y. P. Feng, J. Ding, L. H. Van and J. H. Yin, *Phys. Rev. Lett.*, 2007, **99**, 127201.
- 20 L. C. Ming, G. H. Quan, X. Xia, Z. Yan, J. Yong, C. Men and Z. X. Tao, *Chin. Phys. B*, 2011, **20**, 047505.
- 21 G. D. Liu, S. L. Ji, L. L. Yin, G. T. Fei and C. H. Ye, *J. Phys.: Condens. Matter*, 2010, **22**, 046002.
- 22 M. Kapilashrami, J. Xu, K. V. Rao, L. Belova, E. Carlegrim and M. Fahlman, *J. Phys.: Condens. Matter*, 2010, **22**, 345004.
- 23 B. M. Maoz, E. Tirosh, M. B. Sadan and G. Markovich, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 161201.
- 24 Q. Li, B. Ye, Y. Hao, J. Liu, W. Kong and B. Ye, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2013, **297**, 29–34.
- 25 S. Zhou, Q. Xu, K. Potzger, G. Talut, R. Grötzschel, J. Fassbender, M. Vinnichenko, J. Grenzer, M. Helm, H. Hochmuth, M. Lorenz, M. Grundmann and H. Schmidt, *Appl. Phys. Lett.*, 2008, **93**, 232507.
- 26 R. Kumari, A. Sahai and N. Goswami, *Prog. Nat. Sci.: Mater. Int.*, 2015, **25**, 300–309.
- 27 L. Yiwei, Z. Qingfeng and L. Run-Wei, *Chin. Phys. B*, 2013, **22**, 127502.
- 28 B. Cord, W. Maass, J. Schroeder, K.-H. Schuller and U. Patz, *Thin Solid Films*, 1989, **175**, 287–293.
- 29 P. Kumar, P. Kumar, A. Kumar, R. C. Meena, R. Tomar, F. Chand and K. Asokan, *J. Alloys Compd.*, 2016, **672**, 543–548.
- 30 D. P. Padiyan, A. Marikani and K. R. Murali, *Mater. Chem. Phys.*, 2003, **78**, 51.
- 31 R. K. Hailstone, A. G. DiFrancesco, J. G. Leong, T. D. Allston and K. J. Reed, *J. Phys. Chem. C*, 2009, **113**, 15155–15159.
- 32 R. Abaira, T. Dammak, A. Matoussi and A. Younes, *Superlattices Microstruct.*, 2016, **91**, 365–374.
- 33 P. C. A. Brito, D. A. A. Santos, J. G. S. Duque and M. A. M. Macedo, *Phys. B*, 2010, **405**, 1821–1825.
- 34 Z. V. Popovic, Z. D. Mitrovic, M. Scepanovic, M. G. C. Brojcin and S. Askrabic, *Ann. Phys.*, 2011, **523**, 62–74.
- 35 S. Phokha, S. Pinitsoontorn and S. Maensiri, *Nano-Micro Lett.*, 2013, **5**, 223–233.
- 36 S. Dogra, N. D. Sharma, J. Singh, H. K. Poswal, S. M. Sharma and A. K. Bandyopadhyay, *High Press. Res.*, 2011, **31**, 292–303.
- 37 J. I. Pankove, *Optical Processes in Semiconductors*, Courier Corporation, 2012.
- 38 S. A. Ansari, M. M. Khan, M. O. Ansari, S. Kalathil, J. Lee and M. H. Cho, *RSC Adv.*, 2014, **4**, 16782.
- 39 S. W. Xue, L. X. Shao and J. Zhang, *Journal of Optoelectronic and Biomedical Materials*, 2009, **1**, 34–41.
- 40 P. Goel, M. Arora and A. M. Biradar, *RSC Adv.*, 2014, **4**, 11351.
- 41 G. Wang, Q. Mu, T. Chen and Y. Wang, *J. Alloys Compd.*, 2010, **493**, 202–207.
- 42 N. Paunovi, Z. D. Mitrovi, R. Scurtu, S. Askrabic, M. Prekajski, B. Matovic and Z. V. Popovic, *Nanoscale*, 2012, **4**, 5469.
- 43 M. Varshney, A. Sharma and H. J. Shin, *Adv. Sci., Eng. Med.*, 2015, **15**, 1–7.
- 44 A. Sundaresan and C. N. R. Rao, *Nano Today*, 2009, **4**, 96–106.
- 45 V. Fernandes, P. Schio, A. J. A. deOliveira, W. A. Ortiz, P. Fichtner, L. Amaral, I. L. Graff, J. Varalda, N. Mattoso, W. H. Schreiner and D. H. Mosca, *J. Phys.: Condens. Matter*, 2010, **22**, 216004.
- 46 R. K. Singhal, P. Kumari, A. Samariya, S. Kumar, S. C. Sharma, Y. T. Xing and E. B. Saitovitch, *Appl. Phys. Lett.*, 2010, **97**, 172503.
- 47 L. R. Shah, A. Bakhtyar, Z. Hao, W. G. Wang, Y. Q. Song, H. W. Zhang, S. I. Shah and J. Q. Xiao, *J. Phys.: Condens. Matter*, 2009, **21**, 486004.
- 48 J. M. D. Coey, M. Venkatesan and C. B. Fitzgerald, *Nat. Mater.*, 2005, **4**, 173–179.
- 49 J. C. Conesa, *Surf. Sci.*, 1995, **339**, 337–352.
- 50 X. Chen, L. Guangshe, S. Yiguo, Q. Xiaoqing, L. Liping and Z. Zhigang, *Nanotechnology*, 2009, **20**, 115606.
- 51 C. D. Valentin, G. Pacchioni, A. Selloni, S. Livraghi and E. Giamello, *J. Phys. Chem. B*, 2005, **109**, 11414.
- 52 A. Bouzoubaa, A. Markovits, M. Calatayud and C. Minot, *Surf. Sci.*, 2005, **583**, 107.





- 53 H. Pan, J. B. Yi, L. Shen, R. Q. Wu, J. H. Yang, J. Y. Lin, Y. P. Feng, J. Ding, L. H. Van and J. H. Yin, *Phys. Rev. Lett.*, 2007, **99**, 127201.
- 54 S. Zhou, Q. Xu, K. Potzger, G. Talut, R. Grotzschel, J. Fassbender, M. Vinnichenko, J. Grenzer, M. Helm, H. Hochmuth, M. Lorenz, M. Grundmann and H. Schmidt, *Appl. Phys. Lett.*, 2008, **93**, 232507.
- 55 X. J. Ye, C. S. Liu, W. Zhong, H. A. Song, C. T. Au and Y. W. Du, *Phys. Lett. A*, 2010, **374**, 496.

