

# UV-Vis studies of 800 keV Ar ion irradiated NiO thin films

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We report the evolution of optical absorption properties of 800 keV Ar ion irradiated NiO thin films through UV-Vis characterization. Our results indicate the existence of both Mott-Hubbard ( $d \rightarrow d$  transition) and charge-transfer ( $p \rightarrow d$  transition) characteristic of NiO. The optical band gap of NiO increases from 3.58 to 3.75 eV when irradiated at the fluence of  $5 \times 10^{14}$  ions  $\text{cm}^{-2}$  but it does not show any remarkable variation upon 800 keV Ar ion irradiation at higher fluences. The refractive index and electron polarizability at different ion fluences have been determined from the optical band gap. Both refractive index and electron polarizability follow an opposite trend to that of the energy gap as a function of ion fluence.

Keywords: *ion irradiation; nanoparticles; UV-Vis spectroscopy; band gap*

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## 1. Introduction

Among wide band gap semiconductor materials, NiO thin films have attracted much attention due to their chemical stability and wide range of technological application possibilities in p-type transparent conducting oxides [1], electrochromic devices [2, 3], solar cells [4], gas sensors [5], p-n junctions with n-type ZnO [6, 7], etc.

Thin films of NiO can be grown by various methods, such as electron beam evaporation [8], pulsed laser deposition [9], sol-gel [10], spray pyrolysis [11], sputtering [12], thermal annealing of Ni film [13], etc. Different deposition techniques may influence the microstructure of the films which would finally affect the properties of the films. In order to control the microstructure of the films, one may tune the deposition parameters. It has also been observed that the post-deposition modifications, such as thermal annealing and/or ion

irradiation, improve the film microstructure as desired by the application.

In recent years, a great deal of research attention has been paid to evaluate the refractive index of semiconducting materials due to their application in integrated optical devices, where the refractive index is the key parameter for designing various devices [14]. There are various parameters influencing the refractive index. The most important is the energy band gap of the material which can be influenced by its microstructure. Several models have been proposed on the basis of energy gap data to calculate the refractive index.

In the present study, we have irradiated NiO films with 800 keV Ar ions and estimated the evolution of band gap at different ion fluences. Then, we calculated the refractive index from the band gap using the appropriate model. Our study indicates that NiO films show both Mott-Hubbard ( $d \rightarrow d$  transition) and charge-transfer ( $p \rightarrow d$  transition) characteristics.

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## 2. Experimental

NiO thin films ( $\sim 150$  nm thick) were deposited on Si substrate by e-beam evaporation technique as described by Mallick *et al.* [15]. The as-deposited films were irradiated at room temperature (RT) by 800 keV Ar ions [15] using a low energy ion beam facility at IUAC, New Delhi [16]. Ion irradiation was done at different ion fluences ranging from  $5 \times 10^{14}$  to  $1 \times 10^{16}$  ions  $\text{cm}^{-2}$ . The optical properties of the pristine as well as irradiated films were studied using diffuse reflectance spectroscopy by a double beam UV-Vis spectrophotometer (Shimadzu, UV-2450) with an integrating sphere assembly.

## 3. Results and discussion

Fig. 1 shows the variation of absorption coefficient ( $\alpha$ ) of pristine and 800 keV Ar irradiated NiO thin films as a function of photon energy. It can be seen from the absorption coefficient that both the pristine and irradiated NiO show several absorption bands within the photon energy of 1.5 to 5 eV. The bands present in the absorption spectra were estimated using the following relation [17]:

$$\alpha = \frac{B(h\nu - E_g)^m}{h\nu} \quad (1)$$

where  $h\nu$  is the incident photon energy,  $\alpha$  is the absorption coefficient,  $B$  is a materials dependent constant and  $E_g$  is the optical band gap. Depending on the nature of transition,  $m$  takes the value  $1/2$ ,  $3/2$ ,  $2$  or  $3$ , respectively [18], for direct allowed, direct forbidden, indirect allowed or indirect forbidden. In the present study, the values of the bands present in the absorption spectra were determined by extrapolating the linear portion of  $(\alpha h\nu)^2$  vs.  $h\nu$  plot to the  $h\nu$  axis for  $\alpha = 0$  (Fig. 2). As indicated from Fig. 2, four bands are present in the pristine as well as in 800 keV Ar ion irradiated NiO films. The absorption band present in UV region is attributed to the optical band gap ( $E_g$ ) of NiO [19]. The transition between oxygen p-states at the valence-band edge and nickel d-states at the conduction band edge [20–22] leads to the optical band gap of essentially charge transfer character [23]. The others ( $E_{g1}$ ,  $E_{g2}$  and  $E_{g3}$ ) are the

characteristic features of  $d \rightarrow d$  excitation energies of NiO surface and bulk as discussed later. In the present case, the optical band gap of NiO has increased from 3.58 to 3.75 eV when irradiated at the fluence of  $5 \times 10^{14}$  ions  $\text{cm}^{-2}$  but it has not shown any remarkable variation with 800 keV Ar ion irradiation at higher fluences. This indicates that the 800 keV Ar ion irradiation does not influence the particle size of NiO upon irradiation above the fluence of  $5 \times 10^{14}$  ions  $\text{cm}^{-2}$ .

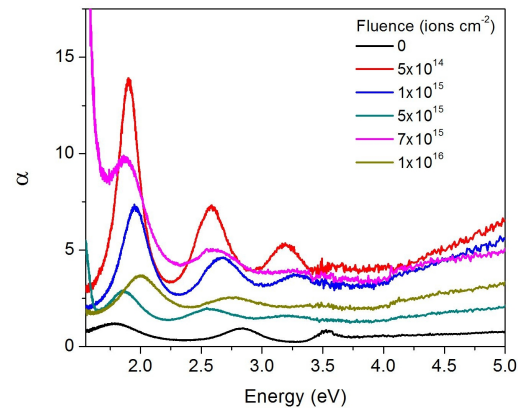


Fig. 1. Variation of absorption coefficient ( $\alpha$ ) of pristine and 800 keV Ar irradiated NiO thin films as function photon energy.

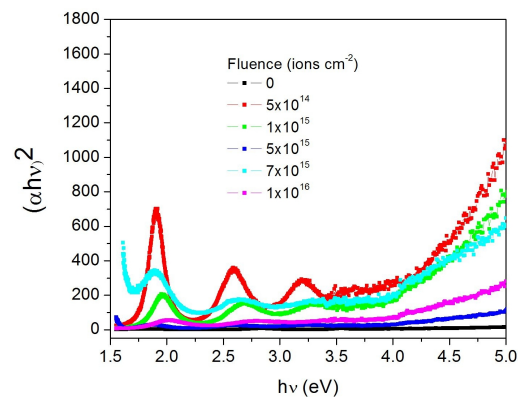


Fig. 2. Variation of  $(\alpha h\nu)^2$  vs. photon energy,  $h\nu$  for pristine and 800 keV Ar irradiated NiO thin films.

Refractive index ( $n$ ) is one of the important properties for evaluation of potential application of the materials in integrated optical devices. The ' $n$ ' depends on various material parameter and band

Table 1. Variation of the values of  $E_g$ ,  $n$ ,  $\alpha'_{\text{classical}}$  and  $\alpha'$  at different ion fluences for NiO films.

Fluence (ions cm <sup>-2</sup> )	$E_g$ (eV)	$n$ as per equation (2)	$\alpha'_{\text{classical}}$ as per equation 3 ( $\times 10^{-24}$ cm <sup>3</sup> )	$\alpha'$ as per equation 4 ( $\times 10^{-24}$ cm <sup>3</sup> )
0	3.58	2.23192	2.52259	2.50604
$5 \times 10^{14}$	3.75	2.19879	2.48177	2.456
$1 \times 10^{15}$	3.71	2.20641	2.49125	2.46766
$5 \times 10^{15}$	3.67	2.21413	2.50081	2.47939
$7 \times 10^{15}$	3.7	2.20833	2.49363	2.47058
$1 \times 10^{16}$	3.72	2.20449	2.48887	2.46474

gap is one of them. There are several models to calculate  $n$  using  $E_g$ . Recently, Kumar and Singh [24] have proposed a model based on experimental data to calculate the value of  $n$  for mixed materials belonging to groups IV, II – VI, III – V semiconductors, insulators, oxides and halides. According this model, the relation between  $n$  and  $E_g$  is given by:

$$n = KE_g^C \quad (2)$$

where  $K = 3.3668$  and  $C = -0.32234$ ,  $n$  is related to the electron polarizability ( $\alpha'$ ) of ions and local field inside the material. According to the classical theory,  $\alpha'_{\text{classical}}$  for a material can be calculated by using Lorentz-Lorentz relation [14]:

$$\alpha'_{\text{classical}} = \frac{(n^2 - 1) M}{(n^2 + 2) \rho} \times 0.395 \times 10^{-24} \text{ cm}^3 \quad (3)$$

where  $M$  and  $\rho$  are molecular weight (g/mol) and density (g/cm<sup>3</sup>) of the substances, respectively. It has also been reported that the value of  $\alpha'$  can be calculated using the following relation [14]:

$$\alpha' = \left[ \frac{12.41 - 3\sqrt{E_g - 0.365}}{12.41} \right] \frac{M}{\rho} \times 0.395 \quad (4)$$

$\times 10^{-24} \text{ cm}^3$

The values of  $E_g$ ,  $n$ ,  $\alpha'_{\text{classical}}$  and  $\alpha'$  at different ion fluences for NiO films are presented in Table 1.

In addition to band gap, UV-Vis spectra give information about several other transitions which exist below the band gap. The existence of spin allowed onsite bulk  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^5 e_g^3)$  [ $^3A_{2g} \rightarrow ^3T_{2g}$ ],  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^4 e_g^4)$  [ $^3A_{2g} \rightarrow ^3T_{1g}$ ] and  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^5 e_g^3)$  [ $^3A_{2g} \rightarrow ^3T_{1g}$ ] excitations [25] has been reported in both optical spectra [26, 27] and in

the spectra of electron energy loss spectroscopy (EELS) [22, 25, 28, 29]. Like bulk transitions, the existence of  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^5 e_g^3)$  one-electron  $^3B_1 \rightarrow ^3E$ ,  $^3B_1 \rightarrow ^3B_2$  and  $^3B_1 \rightarrow ^3A_2$  transitions and  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^4 e_g^4)$  two-electron  $^3B_1 \rightarrow ^3E$  transition for NiO have also been revealed by EELS spectra [23]. Tables 2 and 3 show the existence of different bulk and surface transitions, respectively, observed in the present study by UV-Vis spectroscopy. The values are matched well with the reported values. Thus, our results are in good agreement with the previously reported  $d \rightarrow d$  excitation energies of the NiO surface and bulk NiO. It is noteworthy to mention here that we do not have information about the  $(t_{2g}^6 e_g^2) \rightarrow (t_{2g}^5 e_g^3)$  bulk and surface transitions as the optical spectra are recorded within the photon energy of 1.5 to 5.0 eV. The appearance of  $d \rightarrow d$  excitations in NiO is due to the large electron correlation effects of partly filled localized 3d shell in solid transition-metal [23, 25, 30]. Our results indicate the existence of both Mott-Hubbard ( $d \rightarrow d$  transition) and charge-transfer ( $p \rightarrow d$  transition) characteristic of NiO [31]. The  $d \rightarrow d$  excited states have energies lower than the charge-transfer excitation, which is important in describing the optical properties of the transition metal oxide (TMO). These low-lying  $d \rightarrow d$  excitations below the gap observed in the present study are of interest for magnetic applications [31].

## 4. Conclusions

Effect of 800 keV Ar ion irradiation on the optical absorption properties of NiO thin films was studied. In addition to optical band gap, our results indicate the existence of both Mott-Hubbard

Table 2. Comparison of observed surface d-d transition energies with the reported values.

	${}^3B_1 \rightarrow {}^3E$	${}^3B_1 \rightarrow {}^3B_2$	${}^3B_1 \rightarrow {}^3A_2$	${}^3B_1 \rightarrow {}^3E$
Reported theoretical value	0.45 [23], 0.46 [23, 32], 0.48, 0.49 [23], 0.50 [23, 32], 0.51 [23], 0.62 [25], 0.83 [33]	0.76, 0.83, 0.88 [23], 0.98 [25], 1.02 [32]	1.04 [32], 1.16 [33], 1.21 [25]	1.17, 1.24 [32], 1.38 [25], 1.44, 1.64 [31], 1.73, 1.83 [23], 1.84 [23, 31], 1.85 [23], 1.87 [33], 1.91 [23], 1.94, 1.95, 1.96 [23], 1.98 [33], 2.55 [32]
Reported experimental value	0.57 [25], 0.60 [29, 34]	1.0 [34]	1.3 [34]	1.6 [29], 1.62 [25], 1.63 [22], 2.18 [35, 36]
Observed in the present study at the Fluence (ions cm <sup>-2</sup> )				
0	—	—	—	1.48, 2.56
$5 \times 10^{14}$	—	—	—	1.75
$1 \times 10^{15}$	—	—	—	1.75
$5 \times 10^{15}$	—	—	—	1.68
$7 \times 10^{15}$	—	—	—	2.18
$1 \times 10^{16}$	—	—	—	1.72

Table 3. Comparison of observed bulk d-d transition energies with the reported values.

	${}^3A_{2g} \rightarrow {}^3T_{2g}$ ( $t_{2g}^6 e_g^2$ ) $\rightarrow$ ( $t_{2g}^5 e_g^3$ )	${}^3A_{2g} \rightarrow {}^3T_{1g}$ ( $t_{2g}^6 e_g^2$ ) $\rightarrow$ ( $t_{2g}^5 e_g^3$ )	${}^3A_{2g} \rightarrow {}^3T_{1g}$ ( $t_{2g}^6 e_g^2$ ) $\rightarrow$ ( $t_{2g}^4 e_g^4$ )
Reported theoretical value	0.74 [23], 0.81 [23, 33], 0.86 [23], 0.96 [30], 1.00 [25]	2.53 [31], 2.55, 2.59, 2.61, 2.66, 2.71 [23], 2.95 – 3.07 [30]	1.46 – 1.59 [30], 1.81 [25], 1.93, 1.97, 2.07, 2.11 [23], 2.14 [33], 2.21 [23], 2.27 [31]
Reported experimental value	1.05 [28], 1.08 [27], 1.10 [25], 1.13 [26], 1.16 [22]	2.75 [22], 2.8 [29], 3.0 [28], 3.04 [26], 3.40 [30]	1.79 [28], 1.86 [27], 1.87 [25], 1.95 [26]
Observed in the present study at the Fluence (ions cm <sup>-2</sup> )			
0	—	2.56, 3.38	1.48
$5 \times 10^{14}$	—	2.83	1.75, 2.27
$1 \times 10^{15}$	—	2.72	1.75, 2.27
$5 \times 10^{15}$	—	2.5	2.14
$7 \times 10^{15}$	—	—	1.5, 2.14
$1 \times 10^{16}$	—	—	1.72, 2.11, 1.21

(d  $\rightarrow$  d transition) and charge-transfer (p  $\rightarrow$  d transition) characteristic of NiO. Refractive index and electron polarizability of pristine and irradiated NiO have been determined from optical band gap. Both these parameters follow opposite trends as compared to the band gap as a function of ion fluence.

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