

SHI irradiation induced amorphization of nanocrystalline tin oxide thin film at low temperature

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ABSTRACT

Nanocrystalline tin oxide (SnO₂) thin films were fabricated using pulsed laser deposition (PLD) technique. The as-deposited films were irradiated at liquid nitrogen (LN₂) temperature using 100 MeV Ag ions at different fluences ranging from 3×10^{13} to 3×10^{14} ions/cm² and at 75° with respect to surface normal. Pristine and irradiated samples were characterized using XRD, AFM, Raman and I-V (current-voltage characteristics) for the study of modifications in structural, surface morphological, bond angle and resistivity respectively. XRD patterns show that the pristine film is highly polycrystalline and irradiation amorphizes the film systematically with increasing the irradiation fluence. The surface of the pristine film contains nanograins of tin oxide with roughness 5.2 nm. Upon irradiation at lower fluences agglomeration is seen and roughness increased to 10.8 nm. Highest fluence irradiation again develops nanograins with roughness 7.5 nm. Raman spectra and I-V characteristics also confirms the irradiation induced amorphization. The observed results are explained in the frame work of thermal spike model. Copyright © 2014 VBRI press.

Keywords: Tin oxide thin film; nanostructures; amorphization; pulsed laser deposition; swift heavy ion irradiation; liquid nitrogen temperature.



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Introduction

Tin oxide is a wide band gap (~ 3.6 eV at 300 K) semiconductor material having high optical transparency in the visible spectrum along with wide variation in electrical resistivity [1]. This material retains its properties such as crystalline phase and band gap in harsh surroundings thus it is very attractive to be used in device fabrication [2, 3]. It is broadly used in three major areas viz. gas-sensing, transparent conductor (as contact electrode) and oxidation catalyst. Recently, amorphous tin oxide thin films, in addition to the crystalline films, have gained considerable attention to be used in transparent electronics [4, 5]. In view of wide variety of suitable properties and large number of applications, different deposition methods have been employed for the fabrication of amorphous and nanocrystalline tin oxide thin films. Among these deposition methods, thermal evaporation, e-beam evaporation, pulsed laser deposition (PLD), R.F. magnetron sputtering, sol-gel method, swift heavy ion (SHI) irradiation etc. have been used successfully for the fabrication of variety of nanostructures of tin oxide thin films [6-14].

SHI irradiation is a unique technique for the modification of materials and for generating surface nanostructures. The spatial selectivity and precise control over the modifications are the uniqueness of modifications induced by SHI irradiation [15]. The earlier studies on SHI irradiation of tin oxide were performed on the nanopowder deducing the fact that it is sensitive to electronic energy loss (S_e) [16]. Mohanty *et al.* [8] showed that phase transformation (amorphous to nano crystalline) of tin oxide occurs when irradiated the initially amorphous tin oxide thin films using 100 MeV Ag ions at room temperature. Rani *et al* [7] concluded that there is dramatic change in crystallinity of tin oxide thin films at different irradiation fluencies when irradiated by 75 MeV Ni ions. All these irradiation experiments were performed keeping the samples at room temperature and normal to the beam. They have studied the basic ion-solid (SHI-tin oxide) interaction effects on the various physical properties such as structural, optical and surface morphology.

The formation of periodic surface structures caused by ion-beam irradiation processes on material surfaces has attracted significant interest for the fabrication of laterally structured materials on a nanoscale. Agarwal *et al* [17] obtained self-affine nano structures on the surface of ZnO thin films. They irradiated evaporated ZnO thin films using 100 MeV Ag ions at different fluencies ranging from 1×10^{10} to 1×10^{13} ions/cm². Surface roughness increases upto a critical fluence and then starts decreasing. Density of surface nanostructures increases upto the fluence of 1×10^{12} ions/cm² due to the reduction in size of nanostructures. The variation in the shape and size of surface nanostructures with surface roughness and density of surface structures was explained using thermal spike model. They concluded that the role of sputtering yield in creation of surface nanostructures at normal incidence can be assumed to be negligible and surface diffusion process is mainly responsible for this. Bolse *et al* [18] observed dewetting of NiO films under SHI irradiation. Dewetting is of strong interest, both from a scientific as well as from technological point of view. Akcoltekin *et al* [19] performed irradiations at grazing incidence to create hillocks on the surface of

SrTiO₃ using 93 MeV and 130 MeV Pb and Xe ions at room temperature. Pivin *et al* [20] studied the processes of nucleation and growth of silver cluster under ion irradiation in ion-exchanged glasses containing no clusters and in sputtered silica films containing 1-2 at. % Ag in which all the metals are precipitated before irradiation. These samples were irradiated with 1.5 MeV He ions, 3 and 100 MeV Au ions at room temperature. They found that nucleation rate is proportional to the product of the reduction cross-section of Ag⁺ ions by the ion-fluence and the process involves the transient formation of Ag₃²⁺ ions. Mohapatra *et al* [21] synthesized Au-Si core-shell nanoparticles embedded in silica matrix by atom beam cosputtering followed by annealing. Optical absorption studies showed regular redshift in localized surface plasmon resonance (LSPR) by controlling the annealing temperature.

We have already studied the nano/ micro-patterning of the surface of NiO thin films on different substrates using 100 MeV Ag ions at LN₂ temperature and at an incidence angle of 75° with the beam axis. AFM images of ion-beam irradiated films show the restructuring of initially flat and coherent NiO film into an almost periodic NiO lamellae structure. We obtained the quite regular lamellae with width, height and average distance of hundreds of nm which are oriented perpendicular to the beam direction [22]. A review on the possibilities of materials modification and nanostructuring by ions of different energies has been discussed by Avasthi and Pivin [15].

Keeping the results of our earlier work in our mind, we have studied SHI irradiation induced amorphization of nanocrystalline tin oxide thin films at low temperature and at grazing angle. In the present study, we have prepared nanocrystalline tin oxide thin films using PLD technique. These films were irradiated by 100 MeV Ag ions at different fluences and further measurements were carried out to study modifications in structural, surface morphological and electrical properties. The changes occurred due to SHI irradiations are explained using the thermal spike model [15]. According to this model, the material is considered as a two component medium viz. the electrons and the atomic lattice. The energetic ion deposits enormous amount of energy to the electron gas and then energy is transferred to the atomic lattice by electron-phonon coupling. The energy transfer occurs in a very short duration ($\sim 10^{-16}$ s or less). Temperature rises very high during the passage of ion through the material along the ion path in a cylindrical region. The hike in temperature is also quenched very soon. Thus, the narrow cylinder of material that was rapidly heated to high temperature transiently and then rapidly quenched by thermal conduction, results in modification of material.

Experimental

Thin films of tin oxide with thickness ~ 100 nm were prepared on Si substrate using PLD technique at UGC-DAE CSR, Indore. The as-deposited films were irradiated with 100 MeV Ag ions at Inter University Accelerator Centre (IUAC) New Delhi at LN₂ temperature. The samples were mounted on a heavy copper ladder with good thermal contact using a thermally conducting adhesive,

ensuring negligible increase in sample temperature during irradiation. The samples were irradiated uniformly at room temperature over an area of $1\text{ cm} \times 1\text{ cm}$ by scanning the ion beam using an electromagnet scanner. The vacuum in the irradiation chamber was $\sim 10^{-6}$ Torr. The irradiation fluence was estimated by measuring the ladder current under secondary-electron-suppressed geometry and taking the scanned ion beam area. The samples were tilted at the angle of 75° with respect to the beam axis. The value of energy of ion is so chosen that electronic energy loss ($S_e = 21.93\text{ keV/nm}$) is much larger than nuclear energy loss ($S_n = 0.13\text{ keV/nm}$). Evidently, the modifications in structural, surface morphological and electronic properties are expected only due to the intense electronic excitation in a very narrow region along the ion path. The irradiated and pristine films have been characterized using XRD, AFM, Raman and current – voltage (I-V) techniques to study the changes in structural, surface morphological and electrical properties induced by irradiation. XRD spectra was recorded using CuK_α radiation at grazing incidence 2° and AFM images were recorded using Nanoscope IIIA atomic force microscopy in tapping mode. Raman spectra were recorded by exciting source Ar with wavelength 514.5 nm and 50 mW power at IUAC, New Delhi, India.

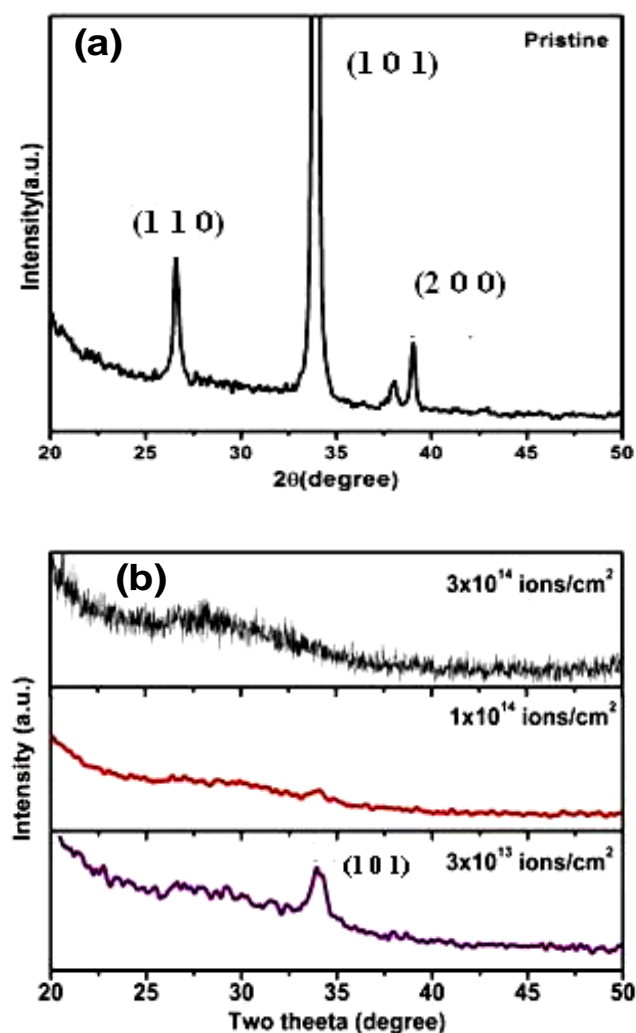


Fig. 1. XRD patterns of (a) pristine and (b) irradiated films at different fluencies.

Results and discussion

XRD analysis

Fig. 1 shows the XRD pattern of as-deposited and irradiated films by 100 MeV Ag ions at oblique incidence of 75° with respect to surface normal. The pristine film is polycrystalline film with cassiterite rutile structure [23]. The average crystallite size of the pristine film was estimated using Scherrer's formula and was found to be 35.48 nm . Successive irradiation has transformed this polycrystalline film into amorphous film. On irradiation at the lowest fluence ($3 \times 10^{13}\text{ ions/cm}^2$), only the dominant peak corresponding to (101) plane is remaining and all other peaks have been disappeared. Further irradiation at middle and highest fluencies, complete amorphization has occurred. This amorphization can be explained on the basis of thermal spike model [24]. When swift heavy ion strikes on the tin oxide, it loses energy via exciting the electrons or ionizing the atoms within few nanometer cylindrical zone along its ion path. This energy is transferred to the lattice via electron-phonon coupling which leads to the generation of large number of defects in the material. Highly dense electronic energy loss deposition along the ion path causes disordering of lattice which leads to amorphization.

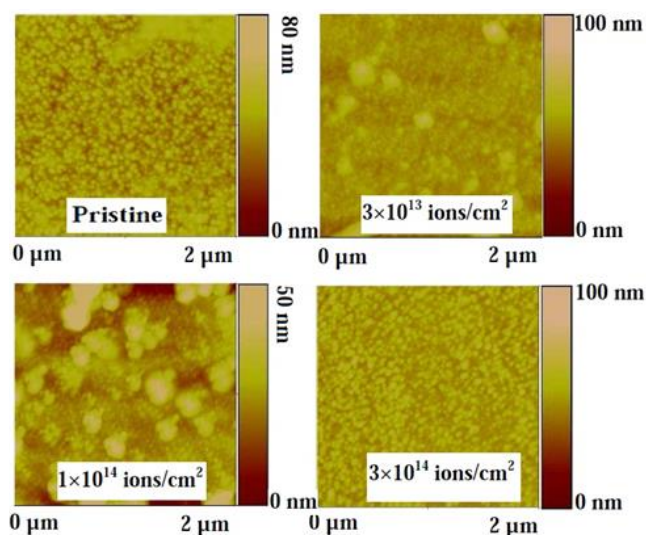


Fig. 2. AFM images of pristine and irradiated films at different fluencies.

AFM analysis

Fig. 2 shows the AFM micrographs of the pristine and irradiated films. The surface of the pristine film has nanograins of tin oxide with average grain size $\sim 82\text{ nm}$ with surface roughness 5.2 nm . Upon irradiation at lowest and middle fluencies (3×10^{13} and $1 \times 10^{14}\text{ ions/cm}^2$), big nanoclusters are seen which implies that at these fluencies, the nanostructures melt and form the big nanoclusters due to agglomeration. At these fluencies, surface roughness increases to 7.5 and 10.8 nm respectively. Highest fluence irradiation ($3 \times 10^{14}\text{ ions/cm}^2$) again develops nanograin with average size $\sim 66\text{ nm}$ with surface roughness 7.2 nm .

The variation of surface roughness with fluence is shown in Fig. 3. The development of surface nanostructures due to the energetic ion bombardment is governed by two competing processes which are sputtering and surface

diffusion. Experimental studies show that the sputtering is dominant in the low energy region whereas surface diffusion becomes dominant in the high energy region [15, 17]. The SHI irradiation induces the formation of nanostructures of regular shape with narrow size distribution at the low fluence due to the strain relaxation. Further irradiation at higher fluences, there is reduction in average size of surface nano structures to ~ 66 nm. The reduction in size of nanostructures upon irradiation at the higher fluences may be due to breaking of bigger grain by the highly dense energy deposition during the ion bombardment.

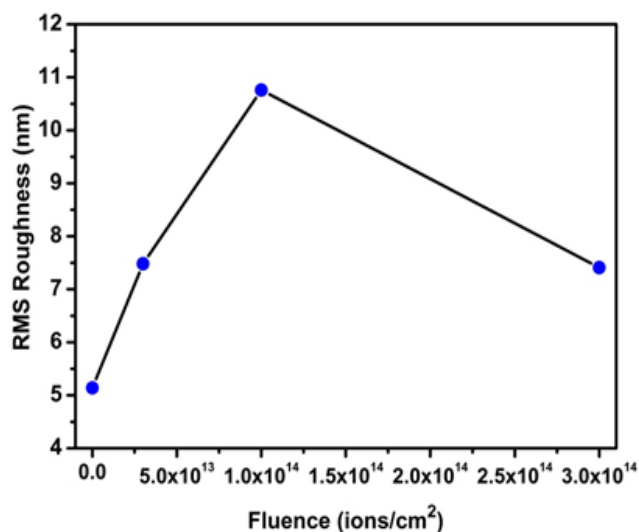


Fig. 3. Variation of surface roughness with fluence.

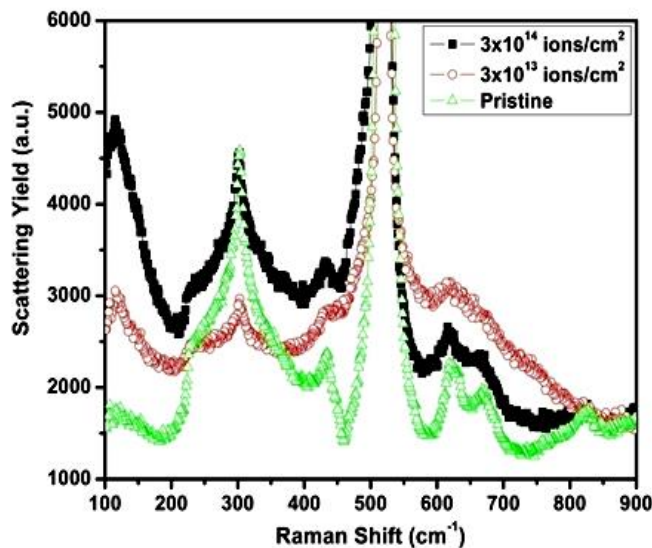


Fig. 4. Raman spectra of pristine and irradiated films.

Raman spectroscopy study

For tin oxide material, the six unit cell atoms give rise to 18 vibrational modes. Out of these 18 modes, two are IR active at 244 or 293 (e_u), 477 (a_{2u}) and 618 (e_u) cm^{-1} , four modes are Raman active at 123 (b_{1g}), 476 (e_g), 634 (a_{1g}) and 778 (b_{2g}) and two are silent. One A_{2u} and two E_u are acoustic [25-27]. Zuo *et al* [27] observed that

nanocrystalline tin oxide has two raman bands centered at 358 (b_1) cm^{-1} and 572 (b_2) cm^{-1} in addition to the raman bands in bulk tin oxide. Fig. 4 shows the Raman spectra of pristine and irradiated films. Pristine film shows the one IR active mode at 300 (e_u) cm^{-1} and three Raman active modes at 460 (a_{2u}), 620 (e_u) and 830 cm^{-1} respectively. The presence of these modes is sufficient to confirm that the as-deposited film is nano crystalline tin oxide. The observed modes are shifted from their actual peak positions which can be due to the strain present in the nanocrystalline film. Irradiation has decreased the intensity of the Raman peaks which indicated the size reduction or amorphization of the crystallinity of the films [28].

Current–voltage characteristics

Electrical properties of all films i.e. pristine and irradiated films were studied by measuring the current as the function of voltage. The plots are shown in the Fig. 5. The pristine film is highly electrical conductive as inferred from the I-V plots. Irradiation has made the film amorphous and thus the conductivity of the films decreases. The irradiation induced decrement in electrical conductivity of tin oxide thin film is due to the scattering of charge carriers from defects and grain boundaries and widening of the band gap. It is well known that the resistivity is related to the carrier concentration and its mobility. Since the film is prepared in the oxygen rich environment, the carrier concentration will be less. Thus the observed value of electrical conductivity in the pristine film is due to the high value of mobility of charge carriers which is being affected by grain boundary scattering and lattice scattering. Irradiation has amorphized the film so that the charge carriers are bounded to the net non-uniform structures. Also the free charge carriers are lowered due to the lattice disorder. These phenomenon leads to the observed decrement in electrical conductivity [29].

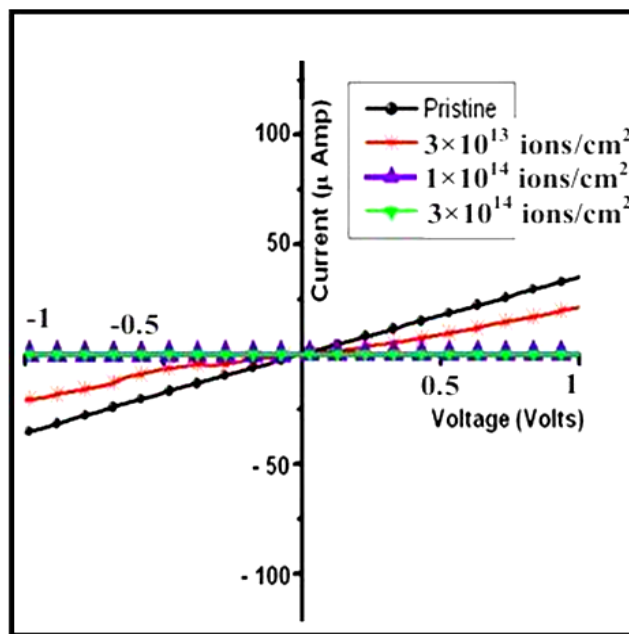


Fig. 5. Current–Voltage (I-V) characteristics of pristine and irradiated films.

Conclusion

Tin oxide films were deposited by PLD method and irradiated using 100 MeV Ag ions at different fluences to study the changes in structural, surface morphological and electrical properties. XRD pattern of the irradiated film showed that amorphization has occurred in the initially nanocrystalline film. AFM images revealed that SHI irradiation deform the nano grains up to the middle fluences irradiation and at highest fluence, the nano grains reappears which are amorphous in nature. I-V characteristics and Raman spectroscopic study reveals that the increasing fluence irradiation has amorphized the film systematically.

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Reference

- Kilic, Cetin; Zunger, Alex; *Phys. Rev. Lett.* **2002**, 88(9), 095501.
DOI: [10.1103/PhysRevLett.88.095501](https://doi.org/10.1103/PhysRevLett.88.095501)
- Batzil, Matthias; Diebold, Ulrike; *Progress in Surface Science.* **2005**, 79, 47.
DOI: [10.1016/j.progsurf.2005.09.002](https://doi.org/10.1016/j.progsurf.2005.09.002)
- Xiang, X.; Zu, X.T.; Zhu, S.; Wang, L.M.; Shutthandan, V.; Nachimuthu, P.; Zang, Y.; *J. Phys.D: Appl. Phys.* **2008**, 41, 225107.
DOI: [10.1088/0022-3727/41/22/225102](https://doi.org/10.1088/0022-3727/41/22/225102)
- Kamiya, Toshio; Hosono, Hideo; *NPG Asia Mater.* **2010**, 2, 15.
DOI: [10.1038/asiamat.2010.5](https://doi.org/10.1038/asiamat.2010.5)
- Keendy, M.K.; Kruijs, F.E.; Fissan, H.; *J. Phys.D: Appl. Phys.* **2003**, 93(1), 551.
DOI: [10.1063/1.1525855](https://doi.org/10.1063/1.1525855)
- Stanimirova, T.J.; Atanasov, A.P.; Dimitrov, G.I.; Dikovska, O.A.; *J. Optoelectron. Adv. Mater.* **2005**, 7, 1335.
- Rani, S.; Puri, N.K.; Roy, C. S.; Bhatnagar, M.C.; Kanjilal, D.; *Nucl. Instr. And Meth. B* **2008**, 266, 1987.
DOI: [10.1016/j.nimb.2008.02.062](https://doi.org/10.1016/j.nimb.2008.02.062)
- Mohanty, T.; Satyam, P.V.; Kanjilal, D.; *J. Nanoscience and Nanotechnology*, **2006**, 6, 1.
DOI: [10.1166/jnn.2006.532](https://doi.org/10.1166/jnn.2006.532)
- Pan, Q.X.; Fu, L.; Dominguez.; *J. Appl. Phys.* **2001**, 89, 6056.
DOI: [10.1063/1.1368866](https://doi.org/10.1063/1.1368866)
- Luo, H.S.; Wan, Q.; Liu, W.L.; Zhang, M.; Di, F.Z.; Wang, Y.S.; Song, T.Z.; Lin, L.C.; Dai, Y.; *J. Nanotechnology*, **2004**, 15, 1424.
DOI: [10.1088/0957-4484/15/11/006](https://doi.org/10.1088/0957-4484/15/11/006)
- Mohanty, T.; Batra, Y.; Tripathi, A.; Kanjilal, D.; *Journal of Nanoscience and Nanotechnology* **2007**, 7, 1.
DOI: [10.1166/jnn.2007.764](https://doi.org/10.1166/jnn.2007.764)
- Kim, W.T.; Lee, U.D.; Chho, C.D.; *J. Appl. Phys.* **2001**, 90, 175.
DOI: [10.1063/1.1372159](https://doi.org/10.1063/1.1372159)
- Tarey, D.R.; Raju, T.A.; *Thin Solid Films* **1995**, 128, 181.
DOI: [10.1016/0040-6090\(85\)90070-7](https://doi.org/10.1016/0040-6090(85)90070-7)
- Min, K.B.; Choi, D.S.; *Sensors and Actuators B* **2004**, 98, 239.
DOI: [10.1016/j.snb.2003.10.023](https://doi.org/10.1016/j.snb.2003.10.023)
- Avasthi, D.K.; Pivin, J.C.; *Current Science* **2010**, 98, 780.
- Hemon, S.; Gourbilleau, F.; Dufour, Ch.; Paumier, E.; Dooryhee, E.; Rouanet, A.; *Nucl. Instr. And Meth. B* **1997**, 122, 526.
DOI: [10.1016/S0168-583X\(96\)00580-0](https://doi.org/10.1016/S0168-583X(96)00580-0)
- Agarwal, D.C.; Chauhan, R.S.; Avasthi, D.K.; Khan, S.A.; Kabiraj, D.; Sulania, I.; *J. Appl. Phys.* **2008**, 104, 024304.
DOI: [10.1063/1.2953177](https://doi.org/10.1063/1.2953177)
- Bolse, T.; Elsanousi Ammar, Paulus Hartmut, Bolse W.; *Nucl. Instr. And Meth. B* **2006**, 244, 115.
DOI: [10.1016/j.nimb.2005.11.053](https://doi.org/10.1016/j.nimb.2005.11.053)
- Akcoltekin, E.; Akcoltekin, S.; Osmani, O.; Duvenbeck, A.; Lebius, H.; Schlegel, M.; *New Journal of Physics*, **2008**, 10, 053007.
DOI: [10.1088/1367-2630/10/5/053007](https://doi.org/10.1088/1367-2630/10/5/053007)
- Pivin, J.C.; Roger, G.; Garcia, M.A.; Singh F.; Avasthi, D.K.; *Nucl. Instr. And Meth. B* **2004**, 215, 373.
DOI: [10.1016/j.nimb.2003.07.002](https://doi.org/10.1016/j.nimb.2003.07.002)
- Mohapatra, S.; Mishra, Y.K.; Avasthi, D. K.; Kabiraj, D.; Ghatak, J.; Varma, S.; *Appl. Phys. Lett.*, **2008**, 92, 103105.
DOI: [10.1063/1.2894187](https://doi.org/10.1063/1.2894187)
- Chauhan, R.S.; Agarwal, D.C.; Kumar, S.; Khan, S.A.; Kabiraj, D.; Sulania, I.; Avasthi, D.K.; Bolse, W.; *Vacuum*, **2011**, 86, 96.
DOI: [10.1016/j.vacuum.2011.04.024](https://doi.org/10.1016/j.vacuum.2011.04.024)
- Chen, Z.; Lai, J.K.L.; Shek, C.H.; Chen, Haydn.; *J. Mater. Res.* **2003**, 18, 1289
DOI: [10.1557/JMR.2003.0176](https://doi.org/10.1557/JMR.2003.0176)
- Toulemonde, M.; Dufour, C.; Paumier, E.; *Phys. Rev. B* **1992**, 46, 14362.
DOI: [10.1103/PhysRevB.46.14362](https://doi.org/10.1103/PhysRevB.46.14362)
- Kar, Ayan; A. S. Michael; Dutta Mitra; Kumari, Jyoti; Meyyappan, M.; *Semicond. Sci. Technol.* **2010**, 25, 024012.
DOI: [10.1088/0268-1242/25/2/024012](https://doi.org/10.1088/0268-1242/25/2/024012)
- Dieguez, A.; Romano-Rodriguez, A.; Vila, A.; Morante, J.R.; *J. Appl. Phys.* **2001**, 90, 1550.
DOI: [10.1063/1.1385573](https://doi.org/10.1063/1.1385573)
- ZuO, J.; Xu, C.; Liu, X.; Wang, C.; Wang, C.; Hu, Y. Qian, Y.; *J. Appl. Phys.* **1994**, 75, 1835.
DOI: [10.1063/1.356348](https://doi.org/10.1063/1.356348)
- Kuiri, P.K.; Ghatak, J.; *Vacuum* **2010**, 85, 135.
DOI: [10.1016/j.Vacuum.2010.04.016](https://doi.org/10.1016/j.Vacuum.2010.04.016)
- Alexandre J.C. Lanfredi; Renau R. Galdes.; Olivia M. Berengue; Edson R. Leite; Adenilson J. Chiquito; *J. Appl. Phys.* **2009**, 105, 023708.
DOI: [10.1063/1.3068185](https://doi.org/10.1063/1.3068185)

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