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Cite this: DOI: 10.1039/c0xx00000x

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## **ARTICLE TYPE**

## Growth of polarity controlled ZnO nanorods array on glass/FTO substrate by chemical bath deposition

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Received (in XXX, XXX) XthXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

We present a polarity controlled ZnO nanorod thin film deposition on glass substrate by Chemical Bath Deposition (CBD). The polarity of ZnO is controlled by the anions of the Zn-salt used in the deposition solution. In presence of  $-SO_4^{2^-}$  the rods grow in +c direction (Zn-polar), while -c directional (O-polar) growth is observed in the presence of  $-NO_3^-$ . The polarity of the nanorod is confirmed by Convergent <sup>10</sup> Beam Electron Diffraction (CBED) technique. The study depicts that the rods with different polarity

beam Electron Diffraction (CBED) technique. The study depicts that the rods with different possess different optical, electrical and chemical properties.

#### Introduction

Zinc oxide is a favorable material in various optoelectronic applications. It is non-toxic, abundant and probably among one of <sup>15</sup> the most-studied materials. It has a high bandgap, large exciton binding energy, high electron mobility and considerably large piezoelectric effect.<sup>1,2,3</sup> ZnO crystallises in wurtzite, zinc-blende and rock salt structure, where wurtzite is the only

- thermodynamically stable phase at ambient conditions<sup>1</sup>. Wurtzite <sup>20</sup> ZnO is a classic example of a polar crystal. In this structure, all Zn atoms are tetragonally coordinated with O atom and vice versa. Hence  $Zn^{2+}$  ions and  $O^{2-}$  ions are arranged alternately along <0002> direction, which is conventionally known as *c*-axis. Due to deformed tetragonal structure and absence of centre of
- <sup>25</sup> inversion, a net dipole moment along the *c-axis* direction is present. When the moment vector is directed from "O" to "Zn" along the +*c-direction*, then the crystal is known as Zn-polar, which can have both Zn and O terminated surface. Therefore polarity is a bulk property while the surface termination is what
- <sup>30</sup> the name suggests. Similar but reverse is applicable when it is Opolar.<sup>4,5</sup> The different polar surfaces exhibit dissimilar growth process, surface electronic properties, and doping density.<sup>6,7</sup> It is found that the material properties, *viz* electrical, chemical and optical, to a large extent also depend on the polarity of the ZnO.

<sup>35 8,9</sup> Thus for reliable device applications, it is important to have adequate control over the polarity of the material.<sup>10</sup> Control over the polarity during the ZnO film growth has been

- previously demonstrated mainly by substrate surface/interface modification.<sup>11,12,13,14</sup> In most cases, ZnO was deposited by 40 molecular beam epitaxy or by sputtering. Selective growth of Znpolar or O-polar ZnO layers are achieved on sapphire either by using thickness-controlled MgO buffer layer<sup>11</sup> or by ultrathin AlN
- interface layer<sup>12</sup>. In some cases, it has also been observed that intermediate layers of Cr-oxide/nitride<sup>15</sup> also controls the polarity <sup>45</sup> of the ZnO films. These template layers are known to lower the
- interface energy for particular polarity and thus help in growth of

desired nanorod polarity <sup>12,15,16</sup>. Apart from templating, Ohashi et al<sup>13</sup> showed that the control over polarity in ZnO can also be achieved by controlling the deposition parameters such as the <sup>50</sup> substrate bias in RF-sputtering. The substrate bias gives an additional energy to the ZnO crystal depending on the orientation of the crystal. Thus one of the two crystal orientation will be energetically favourable and have high nucleation rate. Not only gas/vapour phase techniques, but solution route is also used for <sup>55</sup> polarity control of ZnO. Consonni et al<sup>14</sup> has recently

- demonstrated polarity-controlled ZnO deposition by CBD on templated substrates.
- Chemical bath deposition (CBD) is one of the solution-based techniques that are widely used to deposit metal oxides/sulfides, 60 particularly on large area in a cost effective manner. ZnO is among the most studied materials grown by CBD that reproducibly deposit single crystalline nanorod thin films, oriented along *c*-direction. Here, we report an easy and reliable method to control the nanorod polarity on (amorphous) glass and 65 (polycrystalline) Fluorine doped tin oxide (FTO) substrate by Chemical bath deposition (CBD), without any templating or intentional substrate or interface modification. The control over ZnO polarity is found to be governed by the anions of the zinc salt in the deposition solution. The polarity is confirmed by 70 convergent beam electron diffraction (CBED) measurement. High growth rate and faster etching rate was observed for O-polar ZnO, while for the reverse polarity lower deposition rate and slow etch rate was witnessed. Distinct differences in the schottky barrier height (SBH) and photoluminescence spectra were

#### **Experimental Methods**

75 observed for the polar faces of ZnO nanorods.

Thin films of vertically aligned ZnO nanorod arrays were grown on glass and FTO coated glass substrate by chemical bath deposition with ethanolamine as complexing agent. All <sup>80</sup> deposition were carried at 85 °C under dark, to avoid any photo(electro)chemical reaction. The deposition solution was prepared from an aqueous bath containing 0.1 M ZnSO<sub>4</sub> or

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Fig 1SEM images of a) Zn-polar ZnO nanorods, b) in inset, planar SEM image c) High magnification SEM image of Zn-polar ZnO nanorod tips d) Bright field TEM image of Zn-polar ZnO nanorods, e) O-polar ZnO nanorods, f) in inset, planar SEM image g) High magnification SEM image of O-polar ZnO nanorod tips h) Bright field TEM image of O-polar ZnO nanorods

 $Zn(NO_3)_2$ , 0.4-0.6 M NH<sub>4</sub>OH and 10% v/v ethanolamine (EA) at 85°C for 40 min. The final pH of the solution was maintained ca.11 by adding additional amount of NH<sub>4</sub>OH. The deposition solution was prepared by adding/diluting the previously prepared <sup>10</sup> respective stock solution except NH<sub>4</sub>OH, which was used fresh from the bottle. The substrates (glass and FTO coated glass) were cleaned thoroughly using isopropanol and DI water. Before any deposition, the surface of the substrate were first activated with 0.5 mM KMnO<sub>4</sub> solution with n-butanol and then thoroughly

- <sup>15</sup> rinsed in DI water.<sup>17</sup> It is to be noted that no or little deposit was found without substrate activation. Substrates were kept slightly inclined to the sidewall of the vial to avoid accumulation of bulk precipitation. Surface faced downwards was chosen for characterization while the other surface was cleaned with diluted
- $_{\rm 20}$  HCl soaked cotton rub. For chemical etching experiments, films were dunked directly into freshly prepared 18 mM HCl solution followed by rinsing with DI water and dried under flow of  $\rm N_2$  gas.

#### Characterization

- <sup>25</sup> The film morphology was studied by scanning electron microscope (JSM-7600F and ZEISS Ultra 55) equipped with inlens secondary electron detector. All measurements were performed with same accelerating voltage. Conducting atomic force microscopy (VeecoNanoScope IV) was used to study the
- <sup>30</sup> surface topography and to measure the current-voltage characteristics of single ZnO nanorod. For electrical measurements doped diamond tip was used as electrode. [1010] on-zone CBED experiments were performed with Tecnai 20 UT

TEM microscope (FEI-make, 200 kV) using spot size 5. The CBED simulations, as a function of specimen thickness (10 nm-200 nm in steps of 2 nm) were performed using JEMS software for assumed ZnO polarity (refer Fig. 3a inset) with following parameters: space group - P6<sub>3</sub>mc; a=0.3250 nm and c=0.5207nm, Zn at (1/3, 2/3, 0) and O at (1/3, 2/3, 0.382) and half-convergence 40 angle ~ 3.8 mrad. Block-wave dynamical calculations with Bethe potential at 200 keV were performed with 100 strong reflections and using PRDW atomic form factors. The CBED experimental

patterns were matched with the JEMS simulations to determine the polarity of the ZnO nanorods. Photoluminescence spectra 45 were measured with 325 nm He-Cd laser source.

#### **Results and Discussions**

The mechanism for ZnO deposition can be written as:

$$Zn^{*^{2}} + 4NH_{3} \rightarrow Zn(NH_{3})_{4}^{2+}$$
  

$$Zn^{*^{2}}orZn(NH_{3})_{4}^{2+}orZn(OH)_{2}(NH_{3})_{4} + 2OH^{-} \rightarrow Zn(OH)_{2}$$
  

$$Zn^{*^{2}} + 2OH^{-} \leftrightarrow Zn(OH)_{2} \leftrightarrow ZnO_{(s)} + H_{2}O$$

ZnO forms a series of intermediates with ammonia and hydroxide <sup>50</sup> depending upon the concentration of Zn<sup>+2</sup>, given pH and temperature. The chemical reactions in aqueous systems are in reversible equilibrium condition and on slight perturbation, the reaction moves towards lower overall free energy of the system. Thus at higher temperature and pH ca. 11, the various <sup>55</sup> intermediates forms metastable zinc hydroxide which readily Cite this: DOI: 10.1039/c0xx00000x

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Fig 2 SEM images of a) as deposited Zn-polar ZnO, b) 5 min etching with 18 mM HCl, c) 8 min etching with 18 mM HCl, d) Planar SEM image of etched Zn-polar ZnO, e) as deposited O-polar ZnO, f) 5 min etching with 18 mM HCl, g) 8 min etching with 18 mM HCl, h) Planar SEM image of etched Opolar ZnO.

dehydrates and results in formation of solid ZnO on the substrate.  $^{18}$ 

- Figure 1 (a-c) shows the scanning electron micrographs of the <sup>10</sup> ZnO nanorod thin film deposited on microscopic glass substrates from a solution containing  $ZnSO_4$  as metal salt. Rods with top hexagonal facets of average diameter of ca. 180 nm (std. deviation 31 nm) and average length of 1  $\mu$ m (std. deviation 60 nm) were found uniformly deposited on the substrates.
- <sup>15</sup> Microscopically a major difference in the structure was noticed when the metal precursor was changed from  $ZnSO_4$  to  $Zn(NO_3)_2$ without altering any other deposition parameter. The film grown in the deposition solution containing sulfate ions have an almost flat hexagonal tip while the film deposited by  $Zn(NO_3)_2$  have
- $_{20}$  pencil like tip with hexagonal facet as shown in the figure 1c and 1g respectively. The rod diameter and length was found to be 270 nm (std. deviation 54 nm) and 2.2  $\mu m$  (std. deviation 162 nm) respectively for ZnO nanorod deposited with Zn(NO<sub>3</sub>)<sub>2</sub>. Distinguished differences in the rod morphology has also been
- <sup>25</sup> observed from the TEM images of individual ZnO nanorod deposited from the two different baths, as shown in figures 1d and 1h. Diameter of individual nanorod remains same throughout the length, when deposited from a deposition bath containing  $SO_4^{2-}$ , on the contrary, for nanorod deposited from the  $NO_3^{2-}$
- <sup>30</sup> bath, the diameter keep decreasing along the length of it and the tip ends in a pencil like contour.
  - As per the crystal growth process is concerned, it is expected to have differences in morphology in Zn and O-polar crystals. For the oxygen terminated Zn-polar ZnO, each oxygen atom has three
- $_{35}$  unsaturated bonds along the *c*-direction, while for the oxygen terminated O-polar ZnO, there is only one dangling bond. Thus considering the above, it can be said that the Zn-polar ZnO will have higher lateral growth mode. In contrast to this, for O-polar

ZnO the growth mode is dominated by the step edges as <sup>40</sup> explained by Kato et al.<sup>19,20,11</sup>. So, it is expected that the Zn-polar ZnO will be flat at the top and certainly morphologically different than the O-polar ZnO. Therefore, by simply looking at the morphology, though early but still, it can be fairly assumed that the nanorods deposited from the sulfate bath can possibly be Zn-<sup>45</sup> polar, while the ones deposited from the nitrate bath could be Opolar.

It has been reported that the growth rate of the Zn-polar ZnO is considerably higher than that of O-polar films<sup>12</sup>. Usually the higher growth rate for Zn-polar ZnO thin films can be explained <sup>50</sup> by the surface limited reaction mechanism. Also, in the deposition from aqueous solution, the growth rate is Zn<sup>+2</sup> ion availability and diffusion limited. The oxygen atom in Zn-polar surface has three dangling bonds in comparison to one such bond on O-polar surface. Thus the ease of Zn<sup>+2</sup> ion addition and hence <sup>55</sup> the growth rate is expected to be higher on Zn-polar surface while omitting the overall reaction mechanism. In CBD, where the crystal growth depends on multiple reaction parameters, it is not thus readily understandable. Eventually what is percieved from here as Zn-polar is having lower growth rate than O-polar ZnO.

<sup>60</sup> When the same films are etched in 18 mM HCl, a distinct difference in etch rate is observed. Figure 2a, 2e show the cross section SEM images of a Zn-polar and O-polar ZnO films deposited from the sulfate and nitrate bath respectively. When the films were etched for 5 min and 8 min sequentially, the Zn polar <sup>65</sup> nanorod length decreases from ca. 940 nm to 840 nm and further down to 740 nm. In comparison, for O-polar ZnO, the nanorod length decreases from ca. 2  $\mu$ m to ca. 1.6  $\mu$ m and finally to ca. 1.3  $\mu$ m. Thus the etch rate for O-polar ZnO is 80-90 nm/min while for Zn-polar ZnO is 20-30 nm/min. It is to be noted that

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Fig 3 a-c) Bright field TEM image of Zn-polar ZnO, [10-10] on-zone experimental and simulated CBED patterns; d-f)Bright field TEM image of O-polar ZnO, [10-10] on-zone experimental and simulated CBED patterns. The specimen thickness (t) values considered for the simulations are indicated

uniform etching was observed, inferring that all the nanorods of a particular film are of identical polarity.

- <sup>15</sup> The above observation certainly attributes to the fact that the chemical nature of the surface promotes the differences in the etching rate. We have previously discussed about the net charge on Zn and O-polar ZnO surface. In that continuation, we can attribute that the etching rate of the O-polar ZnO would be higher
- <sup>20</sup> than the Zn-polar. The dangling electrons on the oxygen surface account for the high etching rate due to their susceptibility to reaction with electron-seeking agents in the etchant. The slower over-all etching rate of the Zn surface is in accord with the absence of any dangling electrons on the Zn surface<sup>21,22,23,24</sup>.
- <sup>25</sup> The polarity of ZnO nanorod was further confirmed by the transmission electron microscopy based Convergent Beam Electron Diffraction (CBED) technique. CBED is a well established and reliable technique to determine point group, structure factor, polarity, defects and dislocations types for
- <sup>30</sup> crystals.<sup>25,26,27, 28</sup> CBED is a quantitative electron diffraction technique where the intensity of the diffractions changes with respect to each other as a function of sample thickness, and can be explained by dynamic scattering theory<sup>29</sup>. So, for non-centrosymmetrical material, the intensity of the Friedel pairs g
- <sup>35</sup> and -g (where g is polar direction in the reciprocal space, eg g = 0002 for ZnO) is very different for dynamic scattering, while the difference in the intensity of g and -g would be less if kinematic scattering is considered. The difference in the intensity variation in (0002) and (0002) diffraction discs originates due to the
- <sup>40</sup> multiple scattering routes<sup>25</sup>. Simple calculations of relative phase change by multiple scattering between weak beams, has been used by Tafto et al<sup>30</sup> and Weber et al<sup>28</sup> to determine the absolute polarity of GaAs. The calculations show that the phase difference is zero for three different reflections and thus they scatter
- <sup>45</sup> constructively in 200 reflections, while the direct scattering for  $(\overline{2}00)$  plane is  $\pi$  out of phase with scattering over the two other

paths and thus they scatter destructively. So, the intensity of central fringe increases considerably for (200) diffraction disc in GaAs as compared to (0002) diffraction disc. Hence, by so comparing the experimental CBED patterns with the simulated patterns performed as a function of specimen thickness, the polarities of non-centrosymmetrical [0001] crystals can be determined.

Since, ZnO have wurtzite structure with deformed tetragonal Zn-<sup>55</sup> O structure, a spontaneous polarization along c-axis is observed, which makes it a non-centrosymmetric material<sup>19</sup>. Asymmetry in the intensity variation across the (0002) and (0002) diffraction discs is seen in the CBED pattern of ZnO, which depends on the zone axis, sample thickness, accelerating voltage of electron, <sup>60</sup> observation temperature and the material involved<sup>31</sup>. For given operating conditions of TEM (such as kV) and specimen conditions (zone-axis and specimen temperature), the (0002) and (0002)intensity variations depend on the sample thickness. Hence, by comparing our experimental CBED patterns with the <sup>65</sup> JEMS simulations performed as a function of specimen thickness, the polarities of ZnO nanorods were determined. As shown in

- figure 3, the experimental CBED patterns are in good match with the simulated CBED patterns. Hence we conclude that the ZnO rods deposited from the sulfate bath grow in +c direction [0001] 70 while the rods deposited from the nitrate bath grows in -cdirection which is direction. Hence, we can conclude that the ZnO nanorod films grown from the sulfate bath is Zn-polar while
- ZnO nanorod films grown from the sulfate bath is Zn-polar while the same when deposited from the solution containing nitrate ions, are found to be O-polar.

#### 75 Optical properties of Zn and O-polar ZnO nanorods:

The Photoluminescence (PL) spectra of ZnO films excited with He-Cd laser is measured, which give insight into the optical and crystalline properties of material. Two dominant emission peaks is seen at room temperature for ZnO, which is for near band edge (NBE) UV emission at around 365 nm, and a broad visible peak centered around 550 nm for defects. From figure 4, it can be seen that, the Zn-polar films have higher NBE emission intensity, and is 76 meV blue shifted from that of O-polar ZnO, which is typical

- <sup>5</sup> behaviour for all the samples prepared. It has been previously observed that the Zn-polar ZnO have better crystallinity than Opolar ZnO and thus gives a sharper NBE emission peak<sup>32,</sup>. We see that there has been numerous photoluminescence studies for polar material like ZnO, GaN, InGaN etc, where the PL spectra for
- <sup>10</sup> polar plane is red shifted with respect to non-polar or bulk material. The red shift in the ultraviolet emission is attributed to the previously proposed spontaneous and piezoelectric built- in potential, strain effects<sup>33</sup> and surface traps states.<sup>32,34,35,36</sup> The nature of the surfaces, like termination, shape, strain, defects etc <sup>15</sup> can account for the surface trap states<sup>37</sup>. It has also been observed
- that there is an anomalous blue shift in UV emission spectra for ZnO nanorods beyond quantum confinement regime.<sup>38</sup> The cathodoluminescence UV emission spectra shift toward lower energy side as the diameter of ZnO nanorods increases and this

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Fig 4 Photoluminescence spectra for Zn-polar and O-polar ZnO films

effect is seen upto nanorod of diameter 620 nm. The nanorod with smaller diameter, have higher surface to volume ratio, thus <sup>25</sup> there is more contribution of the non polar surface in the bulk PL spectra. In our sample, the Zn-polar nanorods have an average diameter of 180 nm, whereas the O-polar nanorods have 270 nm. Thus it can be seen that the blue shift in the UV emission spectra of Zn-polar nanorod is due to the smaller diameter.

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#### Electrical properties of Zn and O-polar ZnO nanorods:

Electrical properties of individual ZnO nanorod are characterized by Conductive Atomic Force Microscopy (C-AFM). Here current-voltage (IV) characteristic of individual nanorod was <sup>35</sup> drawn between two electrodes; FTO substrate and conducting diamond coated AFM tip. For these measurements, films were deposited on FTO (F:SnO2) coated glass substrates. For consistency in measurements; electrical contact between tip and the sample was carefully controlled by keeping the landing force

 $_{\rm 40}$  of the diamond-coated tip to 12 nN (low).



Fig 5 Typical IV curve for individual Zn-polar and O-polar ZnO nanorod

All measurements were performed in contact mode of operation. The schottky barrier analysis was performed only for the forward 45 bias section. Here we have aimed to differentiate the effect of the polarity while considering the other factors like interface-states, bulk vacancy etc. to be constant. Thus instead of the magnitude, we have focused on the differential values. As the ZnO was deposited on FTO coated glass substrate, we have considered that 50 the fermi level was pinned to the FTO for both the samples. Hence the nature of the characteristics was governed by the AFM tip to ZnO nanorod contacts. The significant differences between the O-polar-ZnO/tip and the Zn-polar-ZnO/tip contact were measured in the forward bias sweep. The knee voltage for 55 forward bias was recorded 1.5 V and 3.0 V respectively (figure 5a). A similar consistent difference was noticed in the reverse breakdown voltage, but for the barrier analysis, we have considered the forward bias characteristics. I-V characteristics of the above junctions were analyzed using Schottky Diode Theory 60 written in the form,

$$I = I_0 \exp(qV / nkT)(1 - \exp(-qV / kT))$$
$$I_0 = SAT^2 \exp(-\phi_h / kT)$$

Where q is the electron charge, n is the ideality factor, k is the Boltzman constant, T is the absolute temperature, S is the contact area (taken as 10 nm<sup>2</sup>)<sup>39</sup>, A is the Richardson constant (A=32 65 A/cm<sup>2</sup>-K<sup>2</sup> for ZnO), and  $\phi_b$  is the Schottky barrier height.



Fig 6 plot of ln(I/1-exp-qV/kT) against V for Zn and O-polar ZnO nanorod

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Figure 6 gives the logarithmic plot of I/[1-exp(-qV/kT]] against V. The saturation current density  $I_0$  was obtained by drawing the intercept of the plots in figure 6, and was found to be in the order of 1.15 x10<sup>3</sup> A/cm<sup>2</sup> for O-polar and 33.9 A/cm<sup>2</sup> for Zn-polar

- 5 nanorods. The schottky barrier height and the ideality factor for Zn-polar were calculated to be 0.41 eV and 13.9 respectively, while these values came out to be 0.29 eV and 22 respectively for O-polar ZnO. As ZnO is a polar material, it is observed that the bound charges available at the surface due to spontaneous
- 10 polarization are not completely compensated by free electrons developed by adsorption of  $H^+/OH^-$  from the deposition bath. This possibly results in enhancement/lowering of electron affinity at O/Zn polar ZnO surface respectively, influencing the schottky barrier height (SBH)<sup>20</sup>. The ideality factor found here was way
- 15 diverted from the ideal diode equation but compatible with the available literature.<sup>7,40,41</sup> Thus a consistent difference in the SBH was found in the O-polar and Zn-polar ZnO which might reflect a distinct surface chemical nature of the respective rods.

#### Conclusions

- 20 Array of Zinc oxide nanorod with controlled polarity was grown on amorphous (glass) and polycrystalline (FTO) substrate by chemical bath deposition. The polarity is controlled by the anionic component of the zinc salt used for deposition. ZnO nanorods deposited with NO<sub>3</sub> salt of zinc have around 4-5 times
- 25 higher acid etching rate, and lower schottky barrier height as compared to ZnO deposited with SO42 salt of zinc. Based on these observations, the polarity of ZnO with NO3 salt is assigned to be O-polar and Zn-polar with SO<sub>4</sub><sup>2-</sup> salt. The polarity was also confirmed by CBED measurements. A distinct difference in the 30 crystallinity of the ZnO nanorods was also observed by PL study.

#### Acknowledgements

SKS thanks financial support from National Centre for Photovoltaic Research and Education (NCPRE) funded by Ministry of New and Renewable Energy (MNRE), Govt. of India.

- 35 The authors thank Director (DMRL) and Group Head (EMG, DMRL) for providing the TEM facilities to perform the CBED experiments. Also, thanks are due to Prof. D. Banerjee (IISc) for 105 his encouragement to this research. DVSR wish to thank Prof. D. Cherns (University of Bristol, UK) and Prof. P. Stadelmann
- 40 (EPFL, Switzerland) for discussions on rotation calibration and polarity by CBED respectively.

#### Notes and references

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- 1. Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho and H. Morkoc, Journal of 50
- applied physics, 2005, 98, 041301. 2. Z. L. Wang, Journal of Physics: Condensed Matter, 2004, 16,
- R829. 3.
- G.-C. Yi, C. Wang and W. I. Park, Semiconductor Science and 55 Technology, 2005, 20, S22.

4.	Y. Sun, D. J. Riley and M. N. R. Ashfold, The Journal of
5	Physical Chemistry B, 2006, <b>110</b> , 15186-15192.
5.	K. Araki, M. Shinohara, K. Saitoh and M. Terauchi, <i>Physical</i>
60	<i>Review B</i> , 2002, <b>65</b> , 115331.
6. 7	J. Park and T. Yao, <i>Journal of Elec Materi</i> , 2013, <b>42</b> , 716.
1.	Teichert C Motz W Anwand G Brauer and X Chen
	Journal of Applied Physics, 2011, <b>110</b> , 052005.
65 8.	R. E. Sherriff, D. C. Reynolds, D. C. Look, B. Jogai, J. E.
	Hoelscher, T. C. Collins, G. Cantwell and W. C. Harsch,
	Journal of Applied Physics, 2000, 88, 3454-3457.
9.	Y. Adachi, N. Ohashi, I. Sakaguchi and H. Haneda, <i>physica</i>
70 10	status solidi (b), 2013, <b>250</b> , 2122-2125.
11.	<i>LO.</i> 1 <i>e</i> , <i>Hanabook of advanced alelectric, plezoelectric and</i>
	Elsevier. 2008.
	H. Kato, K. Miyamoto, M. Sano and T. Yao, <i>Applied Physics</i>
	Letters, 2004, 84, 4562-4564.
75 12.	X. Wang, Y. Tomita, OH. Roh, M. Ohsugi, SB. Che, Y.
	Ishitani and A. Yoshikawa, <i>Applied Physics Letters</i> , 2005, <b>86</b> , 011021
12	U11921. I P. Williams H. Eurukawa, V. Adashi, S. Grashav, F.
13.	Sondergård and N. Ohashi. Applied Physics Letters, 2013
80	<b>103</b> . 042107.
14.	V. Consonni, E. Sarigiannidou, E. Appert, A. Bocheux, S.
	Guillemin, F. Donatini, IC. Robin, J. Kioseoglou and F.
	Robaut, ACS Nano, 2014, 8, 4761-4770.
15.	J. Park, S. Hong, T. Minegishi, S. Park, I. Im, T. Hanada, M.
85	Cho, I. Yao, J. Lee and J. Lee, <i>Applied physics letters</i> , 2007, <b>00</b> , 201007, 201007, 201003
16	7 Mei X Du V Wang M Ving Z Zeng H Zheng I Jia
10.	O. Xue and Z. Zhang. Applied Physics Letters. 2005, 86.
	112111.
90 17.	M. Kokotov and G. Hodes, Journal of Materials Chemistry,
	2009, <b>19</b> , 3847-3854.
18. 19.	S. Xu and Z. L. Wang, <i>Nano Research</i> , 2011, <b>4</b> , 1013-1098.
	H. Matsul and H. Labata, Lateral Surface Nanowires and
	Publisher 2010
20.	T. Yao and D. SK. Hong. Springer Berlin Heidelberg. Berlin.
	1 edn., 2009.
21.	SC. Han, JK. Kim, J. Y. Kim, KK. Kim, H. Tampo, S.
	Niki and JM. Lee, Journal of the Electrochemical Society,
100	2010, <b>157</b> , D60-D64.
22.	M. Mehta and C. Meier, <i>Journal of The Electrochemical</i>
23	H Tampo P Fons A Yamada K-K Kim H Shihata K
23.	Matsubara, S. Niki, H. Yoshikawa and H. Kanie. Annlied
105	Physics Letters, 2005, 87, 141904.
24.	A. N. Mariano and R. E. Hanneman, Journal of Applied
	<i>Physics</i> , 1963, <b>34</b> , 384-388.
25.	D. P. Nicholls, R. Vincent, D. Cherns, Y. Sun and M. N. R.
	Ashtold, Philosophical Magazine Letters, 2007, <b>8</b> 7, 417-421.
110 20.	G. Fenillet Nanotechnology 2012 23 125702
27	S. Founiei, <i>numbiconnology</i> , 2012, <b>25</b> , 125702. S. Guillemin, L. Ranenne, H. Roussel, F. Sarioiannidou, G.
- / .	Brémond and V. Consonni, <i>The Journal of Physical Chemistry</i>
	<i>C</i> , 2013, <b>117</b> , 20738-20745.
115 28.	Z. Liliental-Weber and L. Parechanian-Allen, Applied physics
	letters, 1986, <b>49</b> , 1190-1192.
29.	H. W. Zandbergen, J. Jansen, A. R. A. Zauner and J. L.
	Weyher, Journal of Crystal Growth, 2000, <b>210</b> . 167-171.

- J. Tafto and J. C. H. Spence, Journal of Applied Crystallography, 1982, 15, 60-64.
- T. Mitate, S. Mizuno, H. Takahata, R. Kakegawa, T. Matsuoka 31 and N. Kuwano, Applied Physics Letters, 2005, 86, 134103.
- 32. D. Oh, T. Kato, H. Goto, S. Park, T. Hanada, T. Yao and J. Kim, Applied Physics Letters, 2008, 93, 241907. 125 33.
  - D. Da-Chao, Z. Jin-Cheng, O. Xin-Xiu, W. Hao, C. Ke, X. Jun-Shuai, X. Sheng-Rui and H. Yue, Chinese Physics B, 2011. 20. 037805.

34.	P. Waltereit, O. Brandt, A. Trampert, H. Grahn, J. Menniger,
	M. Ramsteiner, M. Reiche and K. Ploog, Nature, 2000, 406,
	865-868.
35.	H. Li, A. H. Chin and M. K. Sunkara, Advanced Materials,

- 2006, 18, 216-220.
   T. Kuykendall, P. J. Pauzauskie, Y. Zhang, J. Goldberger, D. Sirbuly, J. Denlinger and P. Yang, *Nature materials*, 2004, 3, 524-528.
- 37. A. H. Chin, T. S. Ahn, H. Li, S. Vaddiraju, C. J. Bardeen, C.-

 10
 Z. Ning and M. K. Sunkara, Nano letters, 2007, 7, 626-631.

 38.
 C.-W. Chen, K.-H. Chen, C.-H. Shen, A. Ganguly, L.-C.

Chen, J.-J. Wu, H.-I. Wen and W.-F. Pong, *Applied Physics Letters*, 2006, **88**, 241905.

- 39. D. Sarid, *Exploring Scanning Probe Microscopy with*
- MATHEMATICA, 2 edn., Wiley-VCH, Berlin, 2007.
   P. Nan, W. Xiaoping, Z. Kun, H. Hailong, X. Bo, L. Fanqing and J. G. Hou, *Nanotechnology*, 2005, 16, 1069.
   W. I. Park, G. C. Yi, J. W. Kim and S. M. Park, *Appl. Phys. Lett.*, 2003, 82, 4358.
- 20

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