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# Influence of cobalt doping on residual stress in ZnO nanorods

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ABSTRACT

Cobalt-doped (0%, 5%, 10%, 15%, and 20%) zinc oxide (ZnO) nanorods were deposited on silicon wafers by a chemical bath deposition technique. Variations in energy band gap and stress due to cobalt doping were analyzed by X-ray diffraction techniques, optical measurements and modeled by density functional theory calculations. Also, the direct residual stress in ZnO nanorods was investigated by measuring the difference in curvature across the doped ZnO thin films deposited on a silicon substrate using the Bow Optic wafer stress measurement system. The stress in doped ZnO films was found to be of compressive in nature. The residual stress in doped ZnO thin films was found in the range of 0.0427–1.0174 GPa. The residual stress was also found to scale with the cobalt doping concentration in ZnO thin film. Also, the crystalline structure of various cobalt doped ZnO nanorods films was confirmed by X-ray diffraction analysis to be of the wurtzite structure. The bandgap of cobalt-doped ZnO was red-shifted from 3.30 eV to 3.21 eV as the cobalt concentration in ZnO nanostructures varied from 0% to 20%. A linear relationship between stress and bandgap shifting in cobalt-doped ZnO nanorods was obtained based on x-ray diffraction and direct stress measurements.

## 1. Introduction

One-dimensional (1D) nanostructures such as nanorods, nanowires, and nanotubes have attracted much attention in recent years due to their potential applications in optoelectronics and energy conversion devices. In the past few years, many nanostructured materials based on various metal oxides, from group III–V and II-VI compound semiconductors were synthesized using low temperature and inexpensive wet chemical techniques [1]. Several unique properties such as wide direct band gap of 3.37 eV and the large exciton binding energy of 60 meV at room temperature make ZnO a highly suitable candidate for applications in optoelectronic devices [2]. Because of a high surface to volume ratio, one-dimensional ZnO nanorods have been regarded as a promising material to improve the absorption in photovoltaic devices [3].

Fabrication of one dimensional ZnO nanorods of high crystalline quality is essential for enhancing the electronic and optical properties of optoelectronic devices. Several methods have been used to synthesize ZnO nanorods such as vapor-phase synthesis [4,5], chemical vapor deposition [6], metal-organic chemical vapor deposition [7,8], which employ deposition at a relatively high temperature ($> 500\,^{\circ}$C). Thus, it is necessary to investigate a simple fabrication technique of ZnO nanorods at the low-temperature condition, which can utilize glass and plastic substrates for broad industrial applications [9]. In this regard, chemical bath deposition method [10,11] has a significant advantage over other techniques due to its relatively low-temperature growth conditions ($< 100\,^{\circ}$C), low cost, and scalability in a deposition.

In photovoltaic technology, it is well known that the residual stress in the film influences not only its mechanical stability but also the electrical parameters of the overlying films [12]. In cobalt doped ZnO, the introduction of a large concentration of cobalt atoms on interstitials sites may bring changes in lattice parameters and influence impurity defect accumulation at grain boundaries. Interstitial atoms and defect states along grain boundaries may also produce stress in the ZnO film [13]. Therefore, measurements and modeling of the residual stress in doped thin films such as cobalt doped ZnO films are timely and of great significance. In the present study, nano-structural aspect contributing to the stress of ZnO nanorods has been studied. In this study, the evolution of stress in ZnO nanorods with cobalt doping is modeled by density functional theory (DFT) and compared to the stress parameters extracted from direct stress measurement technique (BowOptic) and XRD analysis.

## 2. Computational details

We performed density functional theory (DFT) calculations using

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the Quantum Espresso suite [14]. The exchange-correlation potential was described by the generalized gradient approximation as proposed by Perdew–Burke–Ernzerhof [15]. Optimized norm-conserving Vanderbilt pseudopotentials [16] were employed to describe the interaction between the core and valence electrons of Zn, O, and Co atoms. The Brillouin zone was sampled for integration using the Monkhorst-Pack scheme [17] in grids of 8 × 8 × 8 **k**-points. The energy cut-off was set at 200 Ry. Increasing the number of **k**-points or the energy cut-off did not result in a significant total energy change.

## 3. Experimental details

Chemicals used in the deposition, zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$], cobalt nitrate hexahydrate [$Co(NO_3)_3 \cdot 6H_2O$], zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], hexamethylenetetramine [$C_6H_{12}N_4$], and monoethanolamine [$NH_2CH_2CH_2OH$] were purchased from Sigma Aldrich (USA). Boron-doped p-type silicon wafers were first cleaned with dilute hydrochloric acid and then sonicate under deionized water, isopropanol, and acetone, and finally washed with deionized water and dried with nitrogen.

### *3.1. ZnO seed layer*

0.1 M solutions of zinc acetate dehydrate with monoethanolamine (MEA) as a stabilizer was prepared in ethanol. The molar ratio of MEA to zinc acetate dihydrate was maintained at 1.0. This solution was stirred for two hours at 70 °C, and the resulting transparent solution was aged for 24 h at room temperature. The solution was then spin-coated on a glass substrate at 2000 rpm for 30 s. This coating process was replicated many times to produce the desired thickness. After every single spin-coating, the samples were preheated at 120 °C for three minutes using a hot plate. Finally, the seeded substrates were annealed in air at 300 °C for an hour.

### *3.2. Chemical bath deposition (CBD) and doping*

ZnO nanorods were grown with an equimolar (0.1 M) aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine. For cobalt doped ZnO nanorods, cobalt nitrate hexahydrate was used as a doping agent with different (5%, 10%, 15%, and 20%) cobalt to zinc molar ratios. The prepared substrate with seed layer was kept in the solution for 6 h at 90 °C. After the chemical bath, samples were rinsed with deionized water and then dried in air. Finally, the samples were annealed in an argon atmosphere at a 300 °C for half an hour.

### *3.3. Characterization*

Morphological study of prepared ZnO nanorods on silicon substrates was done by FEI Inspect S50 scanning electron microscope (SEM). Crystal structures of undoped and various cobalt doped ZnO nanorods were performed by Rigaku X-ray diffraction (XRD) spectrometer (CuKα radiation, $\lambda = 1.54056$ Å). The thickness and the band gap of ZnO nanostructures were measured using n&k 1200 Analyzer. Stress in ZnO thin films was measured directly using the BowOptic 208 Wafer Stress Measurement system. The UV–vis absorption spectra of ZnO nanorods samples were measured by using a VARIAN Cary 50 Scan UV–visible spectrophotometer.

## 4. Results and discussion

### *4.1. Density functional theory (DFT) calculations*

Using the lattice parameters found experimentally for each of the cobalt concentrations in the respective wurtzite ZnO systems, we relaxed all the atomic positions to equilibrium until no forces were larger than 0.005 eV/Å. The computational modeling does not obtain the exact experimental results, but we observe a similar trend (Table 1). We also modeled ZnO systems with 0% cobalt concentration at each of the lattice parameters and found that the compressive stress is not due to the change in lattice constants but rather to the inclusion of cobalt.

**Table 1**
Average stress and energy band gap calculated using density functional theory.

| Cobalt concentration (%) | Average stress σ (GPa) | Band gap (eV) |
|---|---|---|
| 0 | − 0.222 | 1.83 |
| 5 | − 1.145 | 1.78 |
| 10 | − 1.920 | 1.72 |
| 15 | − 2.847 | 1.67 |
| 20 | − 3.785 | 1.63 |

The calculated energy band gap values obtained with normal DFT are significantly smaller than those observed in the experiment. We obtained bandgap energy of 0.864 eV for the ZnO systems with 0% Co concentration, which is only about 26% of the experimentally measured band gap. All-electron implementations of DFT along with the GW approximation [18] and the Hubbard DFT + *U* methodology [19] can better account for the repulsion of tightly-bound electrons (such as those in the *3d* states of Zn) [20] and thus obtain band gaps closer to the experimental values. Thus, we use the Hubbard DFT + *U* implementation to calculate the band gap energy for the systems and observe a similar trend as a function of the cobalt concentration. The on-site correction for the *3d* states of cobalt used was $U - J = 2.0$ eV. Similarly, $U - J = 7.5$ eV was used for the Zn *3d* states. The calculated energy band gap for the ZnO systems with 0% Co concentration is 1.83 eV, as in Ref. [20], smaller than the value found experimentally but more significant than the value obtained with traditional DFT. We also modeled ZnO systems with 0% cobalt concentration at each of the lattice parameters (Table 1) and found that the band gap value does not change significantly with the change in lattice constants but rather due to the inclusion of cobalt.

### *4.2. Direct stress measurement of ZnO films*

The residual stress in doped and undoped ZnO nanorods film was measured using the Bow Optic wafer stress measurement system. The direct stress profile obtained was compared to stress parameters obtained from XRD measurements. This Bow Optic stress measurement is based on Stoney's equation [21,22]:

$$\sigma = \frac{E_s D_s^2}{6(1-\vartheta_s)} \frac{1}{d_f R}; \tag{1}$$

where $E_s$ and $\vartheta_s$ are Young's modulus and Poisson's ratio of the substrate respectively. $D_s$ and $d_f$ are the substrate and film thickness. R is the curvature of the wafer.

Initially, the bare silicon wafer was scanned, and the background curvature was measured. Then, ZnO nanorods were deposited on the same wafer and scanned to measure the curvature after each deposition. Fig. 1(a) and (b) shows SEM images of 10% and 15% cobalt doped ZnO nanorods. ZnO nanorods thickness was controlled to have almost the same average thickness (≈ 1.13 µm) in all samples, to rule out the effect of variation in film thickness on residual stress. Fig. 1(c) shows the thickness variation in ZnO nanorods with 0–20% cobalt concentration. As the cobalt concentration is increased, the average diameter of the ZnO nanorods increased (from 87 nm to 131 nm), while the density marginally decreased. The cobalt dopant can create complexes with hydroxide in the precursor solution. The reduced reaction between $Zn^{++}$ and $OH^-$ can prevent the overall heterogeneous nucleation process. Since cobalt doped samples have a lower nucleation rate than the undoped ZnO, lateral growth is promoted, increasing the size of the nanorods of the cobalt doped samples [23]. Several previous studies [24–26] indicate that the growth of ZnO nanorods was initiated by the