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luizno.bjp@gmail.com
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Kurhekar, Anil; Apte, Prakash R.; Duttagupta, Siddharth
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CONDENSED MATTER

Growth and Characterization of High-Quality Dielectric Sputtered Zinc Oxide Films from the First Principle

Anil Kurhekar · Prakash R. Apte · Siddharth Duttagupta

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Abstract In this article, we investigate the effect of thermal treatment on a piezoelectric material, zinc oxide, which has found numerous applications in sensors and actuators. Even though the exact mechanisms rendering electrical properties are less known, we suspect that the thermal treatments are responsible for improvement of electrical characteristics of the deposited thin films. We establish that the thermal agitation is responsible for improvement of orders of magnitude in electrical characteristics of sputtered ZnO thin films. The surface quality of the thin films deposited is process dependent. ZnO films were deposited using a dielectric sputtering method, on oxidized silicon 100 n-type wafers. Further, these films were thermally annealed in oxygen ambient at 600 °C in a tube furnace with 2 mL/min pressure. It is observed that, after thermal annealing, the quality of the films is improved by orders of magnitude. The luminance, crystalline quality, and surface morphology of these thin films was measured with atomic force microscopy, scanning electron microscopy with BSD detector (BSD-SEM), and Fourier transform infrared spectroscopy (FTIR). The results infer that the film's surface is very smooth and dense. The surface roughness is improved by 1.3149 nm from 7.882 nm prior to thermal annealing to post-annealing surface roughness with 6.5671 nm. Post-thermal annealing process reveals average grain size was 50 nanometers; the surface roughness is reduced to 6.5671 nm. A significant improvement in electrical current-voltage characteristics was recorded with I-V curve. It is suspected to be due to substantial enhancement in electrical conductivity as a result of thermal treatment and improved spectral response recorded a FTIR peak shift of 1 wave number in total. The FTIR peak shift is suspected to be due to evaporation and reduction in oxygen vacancies due to thermal annealing process. The post-annealed ZnO films will be used for actuation in the future.

Keywords ZnO film · Dielectric sputter · AFM · Scanning electron microscopy · Fourier transform infrared spectroscopy

A. Kurhekar (✉) · P. R. Apte · S. Duttagupta
Department of Electrical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
e-mail: askurhekar@gmail.com

1 Introduction

Because ZnO has abundant sources, low prices, nontoxic characteristics, high-temperature resistance, and chemical stability, it has become an extremely important photoelectric, piezoelectric thin film material [1]. The impact of near surface point defects on ZnO interfaces have been studied by Doutt et al. [2]. Common ZnO thin film production methods include spray pyrolysis [3], photochemical vapor deposition [4], metal organic chemical vapor deposition [5], sputtering methods [6], thermal oxidation [7], and sol-gel methods [8]. Because the sputtering method is nonpolluting and exhibits superior thin film adhesion, flexibility in changing the partial pressure ratio of reactive gases, and stoichiometric quantities that effectively control thin film growth, it is currently the most commonly studied ZnO thin film preparation method.

The electromechanical coupling property has made zinc oxide one of the most attractive materials in MEMS technology [9–16]. In recent years, many piezoelectric sensors/actuators based on bulk and thin films have been presented. Compared to other piezoelectric materials, ZnO film also has good piezoelectric quality, and its microfabrication does not need processing at very high temperature. Hence, ZnO film-

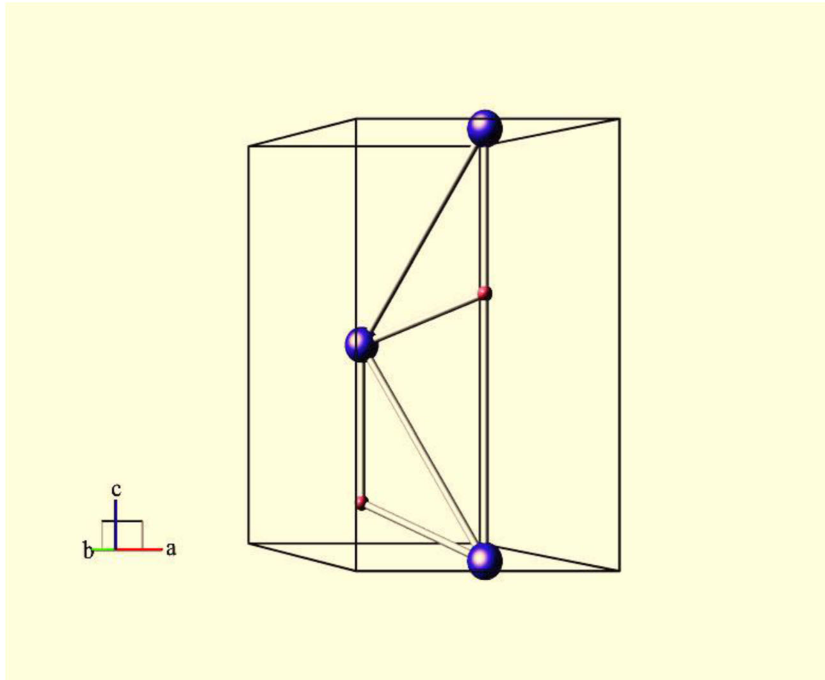


Fig. 1 The ball and stick model of zinc oxide

based piezoelectric sensors/actuators are being designed [13–16]. There is abundant literature about the fabrication and characterization of ZnO films in the past decades. However, few reports presented the quality of ZnO film quantitatively. In the future, this ZnO film will be used in development of MEMS actuator.

2 Zinc-Oxide: A Mechanical Material

ZnO is an element from a space group 186 with standard Hermann-Maguine symbol P63 m c with a=3.2488 nm, b= 3.2488 nm, and c=5.2054 nm with $\alpha=\beta$=90° and γ=120°. The ball and stick model is shown in Fig. 1.

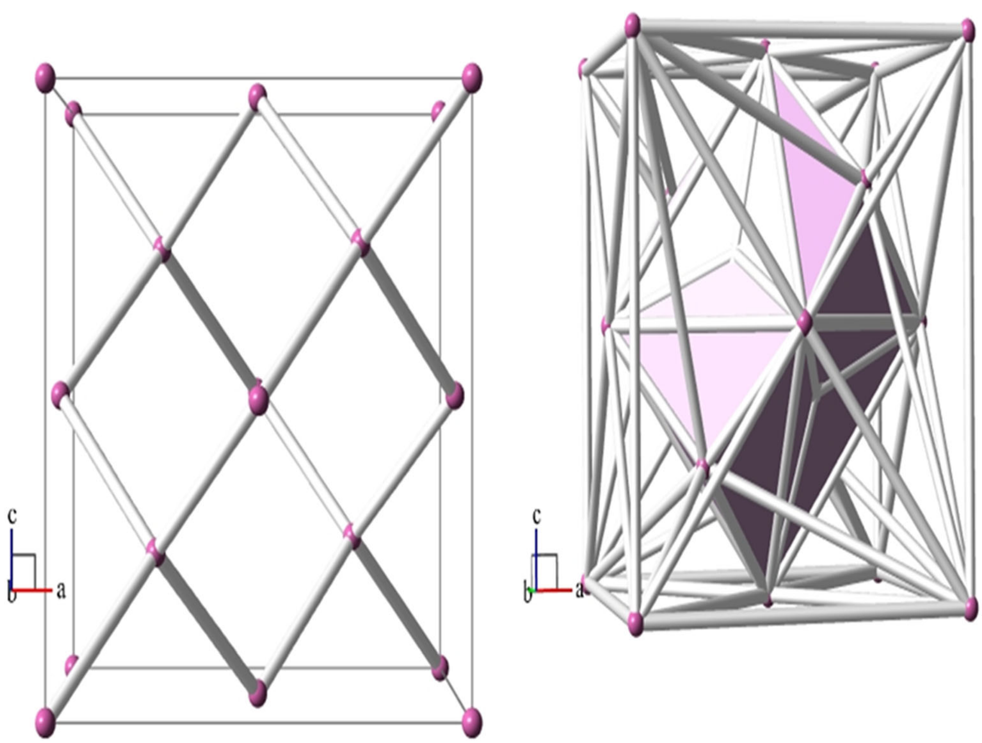


Fig. 2 The ball and stick model of silicon

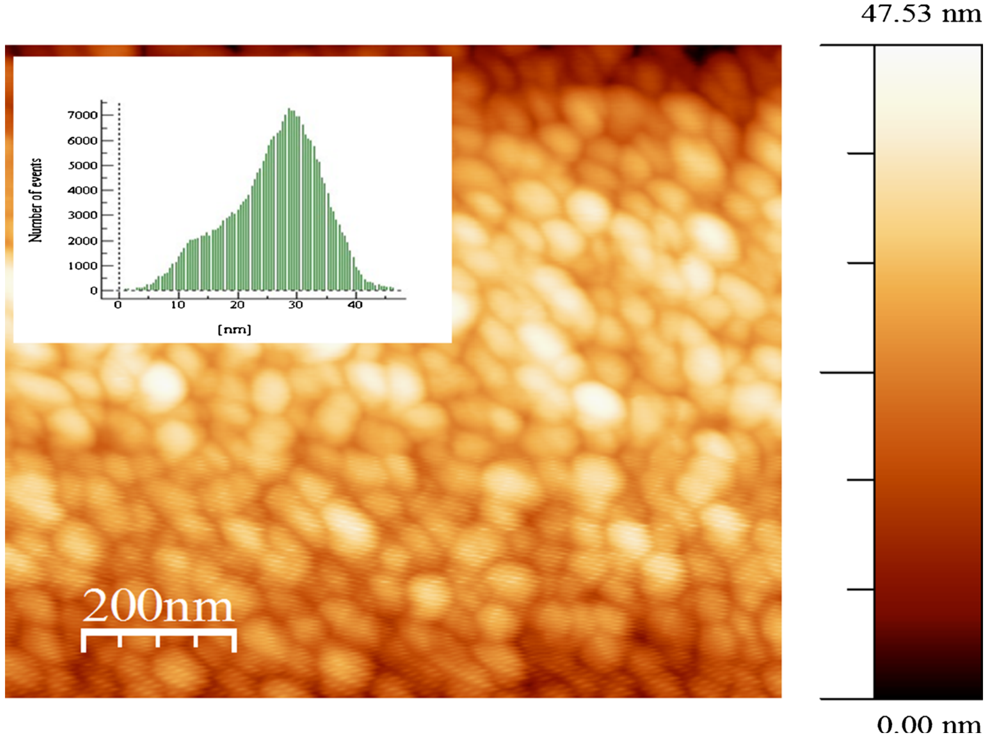


Fig. 3 shows the 2D AFM topographical image and the roughness analysis of the ZnO film before thermal annealing

Si is element from a space group 227 with standard Hermann-Maguine symbol F d -3 m with $a=b=c=5.43$ nm with $\alpha=\beta=\gamma=90°$. The ball and stick model is shown in Fig. 2.

ZnO is a key technological material for MEMS devices. The lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and

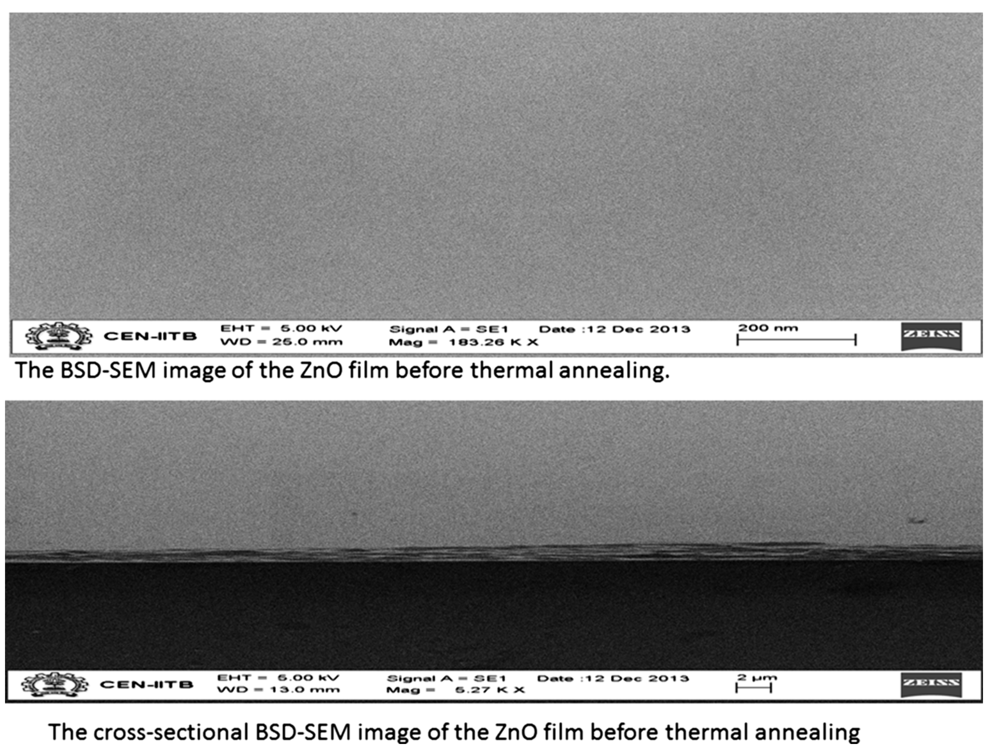


Fig. 4 The BSD-SEM and cross-sectional BSD-SEM image of the ZnO film before thermal annealing

the consequent use of ZnO in mechanical actuators and piezoelectric sensors.

3 Experimental Details

ZnO films were deposited by dielectric sputtering system using an indium bonded ZnO target (99.99 %) with a diameter of 5 in. and a thickness of 3 mm. The substrate comprised n-type silicon (100) with a SiO_x layer. The thickness of the SiO_x layer was 0.5 μm. The target and the SiO_x/Si substrate were then mounted in a dielectric sputtering system to deposit the 75-nm ZnO on top of the SiO_x layer. After the system had been evacuated to a base pressure of 2.2×10^{-5} mbar, the ZnO sputtering was done at a working pressure of 2×10^{-2} mbar. The other preparation conditions are as follows: deposition time=15 min, RF power=150 W, deposition rates=5 nm/min, and gas mixing ratio of O_2/Ar=1/8. The chamber was pumped down to 2.2×10^{-5} mbar using a molecular pump before introducing Ar gas. The above deposition condition was from our previous optimization results. These films were thermally annealed in O_2 ambient at 600°, at the pressure of 2 mbar, for 15 min. The chemical composition and the stoichiometry of the ZnO films were analyzed with the Scanning Electron Microscope that is equipped with BSD detector. The surface morphology of the ZnO film was measured by AFM. The multilayered cross sections of the ZnO films were observed by EVO SEM. Fourier transform infrared spectra using Spectrum 100 Optica FTIR system were obtained for studying spectral behavior.

4 Results and Discussion

As can be seen in Fig. 3, the grain sizes in the ZnO film are very uniform, and the surface is very dense and smooth. The roughness analysis [7] from the AFM showed that the surface roughness (RMS value) is just 7.83 nm. The texture of the ZnO film can be seen in SEM micrograph using Carl Zeiss EVO 18 system in Fig. 4 and cross-sectional morphology of the multilayer structure of the ZnO was observed by SEM. It clearly shows that the ZnO film is polycrystalline. It also shows that the thickness of the ZnO film is about 75 nm. Further, from the cross-sectional study of the interface, it is obvious that the ZnO layer has not diffused into the SiO_x layer. Figure 5 depicts clearly the ZnO film structure with the *x*-profile indicating peaks and valleys. Figure 6 depicts the fourier transform infrared spectra using Spectrum 100 optica FTIR system indicating the high transmittance in the visible range. Figure 7 depicts the AFM topographical image of the ZnO film with the *x*-profile after thermal annealing in O_2 ambient for 600 °C. The rms roughness (*R*q) is 7.82 nm and the difference *R*p–p between the lowest and highest points on the surface is 58.21 nm. Scans

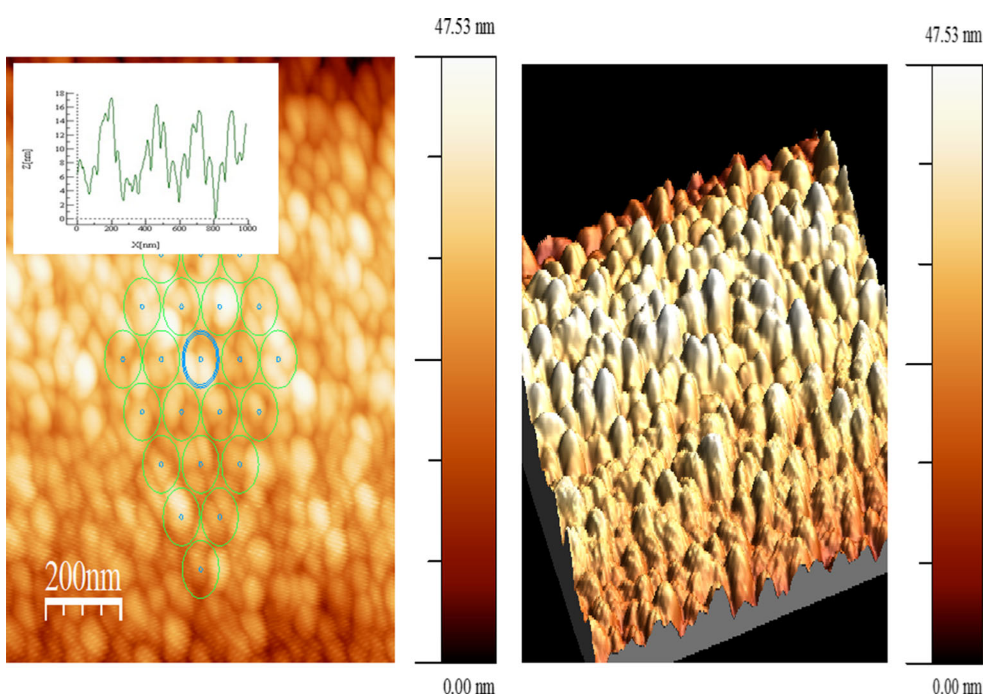


Fig. 5 The AFM topographical image of the ZnO film with the *x*-profile before thermal annealing

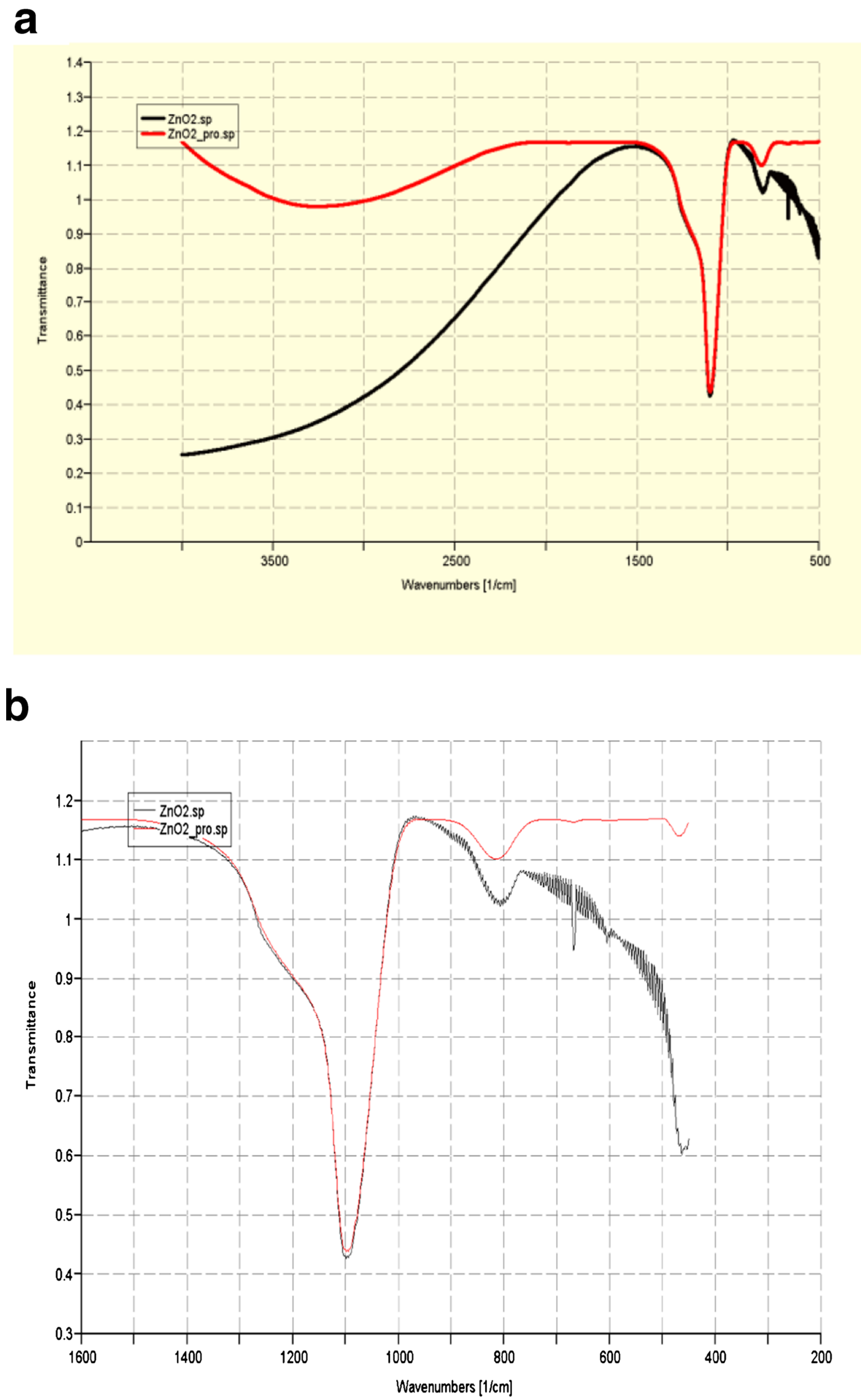


Fig. 6 **a**, **b** The FTIR spectra of the ZnO film subtracted from the oxide background before and after thermal annealing

over 600×600 nm for thermally annealed sample, were also taken and shown in Fig. 7. In this case, roughness *R*q was found to be 6.56 nm and *R*p–p was found to be 53.54 nm, respectively. Thus, it is concluded for our ZnO samples that as the crystalline size increases, the surface roughness increase and vice-versa.

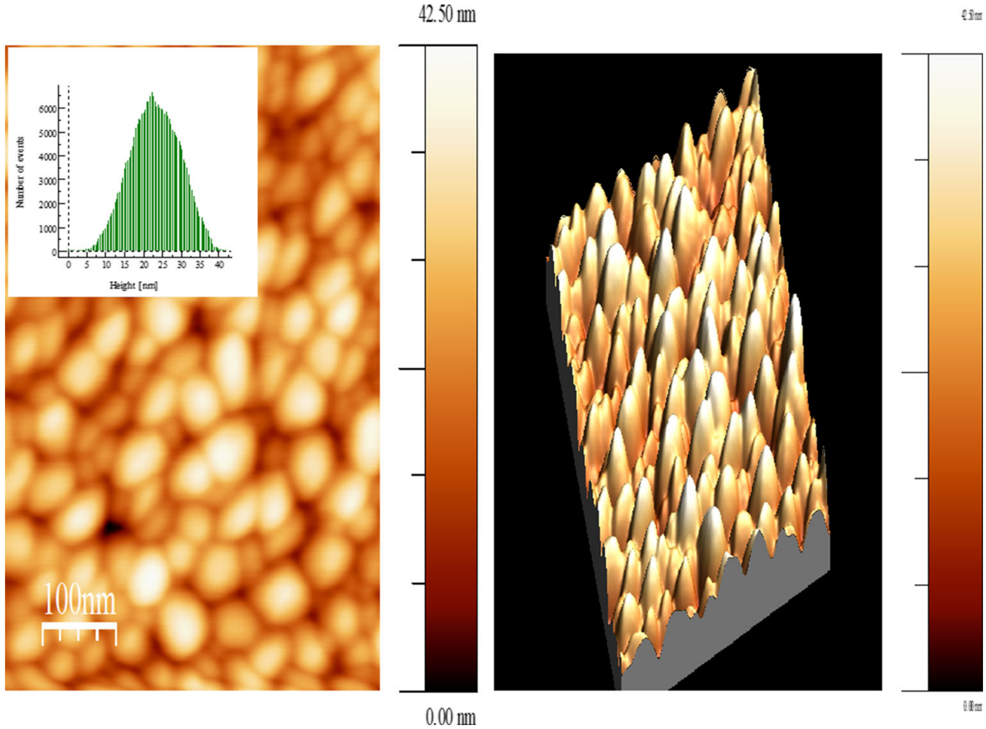


Fig. 7 The AFM topographical image of the ZnO film with the *x*-profile after thermal annealing in O_2 ambient for 600 °C

Figure 8 indicates the surface and cross-sectional BSD-SEM micrographs, after thermal annealing. The detailed study of the cross-sectional BSD-SEM reveals that there is an evidence of formation of nanostructures diffused in SiO_x layer. The annealing in O_2 ambient results in the oriented ellipsoidal swollen grains of ZnO, with enhancement in grain size. After thermal annealing, .the average grain size was 50 nanometers. Figure 9 indicates the current-voltage characteristics of ZnO nanostructures after thermal annealing treatment. Figure 10 depicts the current-voltage characteristics of the ZnO film

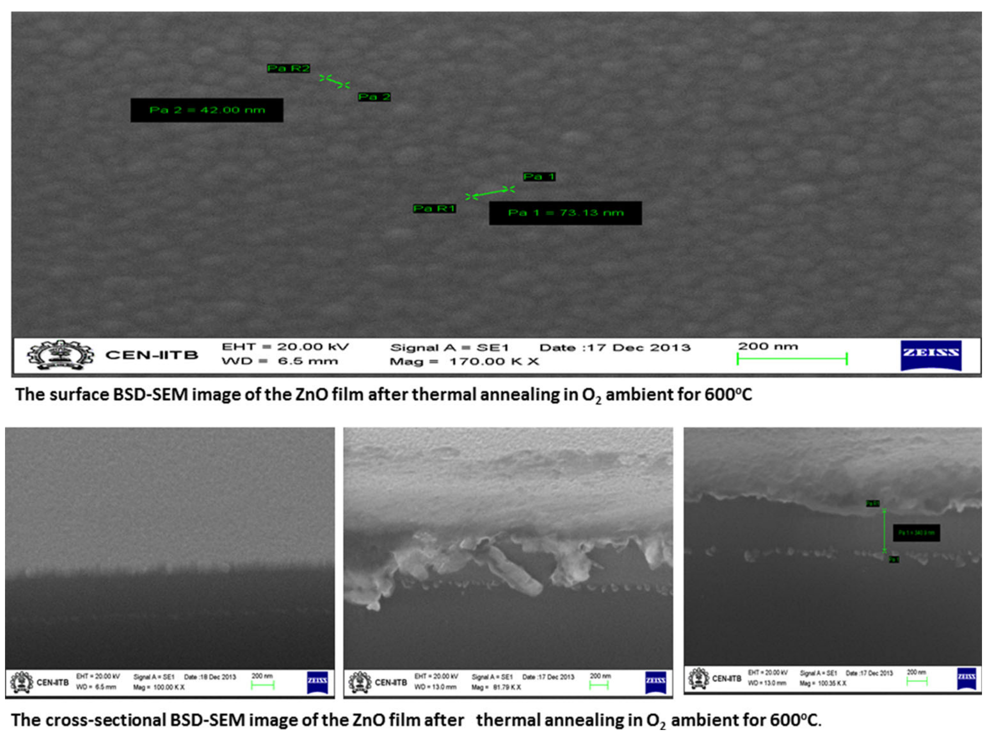
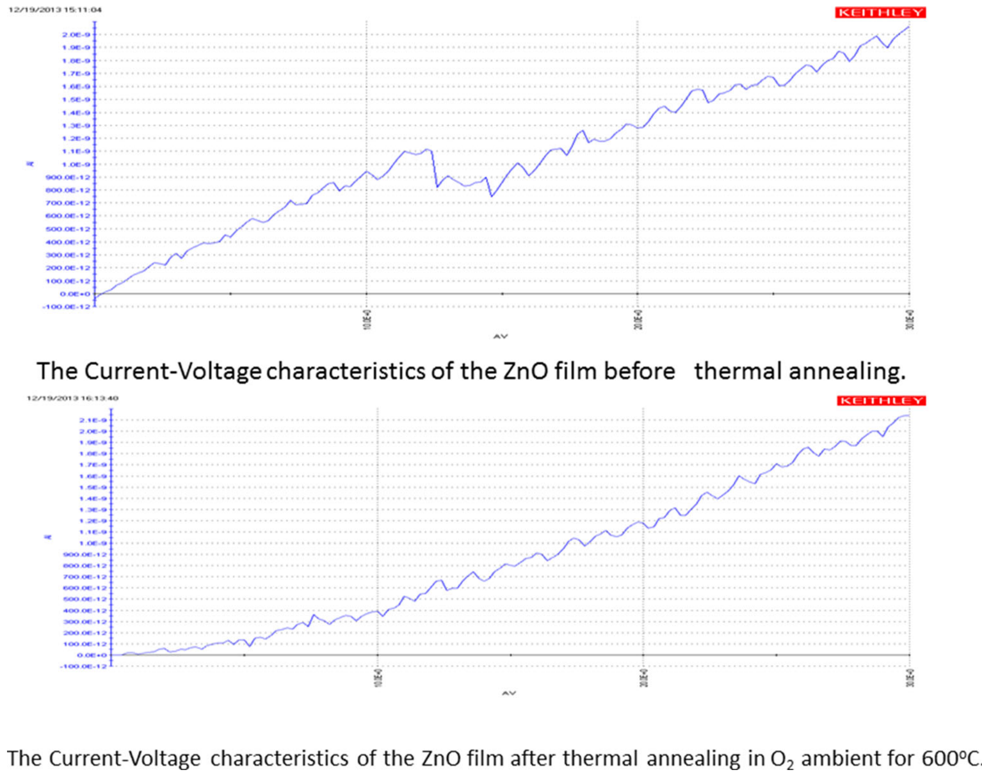


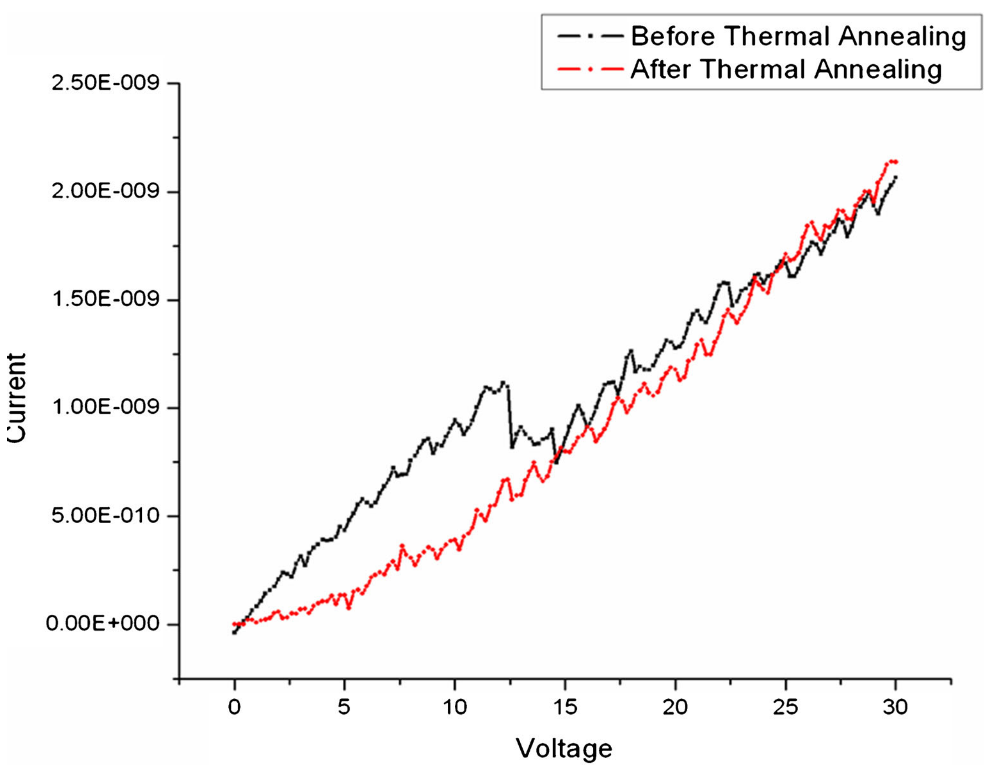
Fig. 8 The surface and cross-section BSD-SEM image of the ZnO film after thermal annealing in O_2 ambient for 600 °C

Fig. 9 The current-voltage characteristics of the ZnO film before and after thermal annealing



before and after thermal annealing in O_2 ambient at 600 °C. The slight break in the linear current-voltage relationship is removed with thermal annealing, resulting in smooth linear relationship between resulting current and the applied voltage. The close observation of FTIR spectra before and after thermal annealing reveals a peak shift of 1 wave number in total. The above characterizations of the ZnO films were just done qualitatively.

Fig. 10 The current-voltage characteristics of the ZnO film before and after thermal annealing in O_2 ambient at 600 °C



Moreover, ZnO films were thermally annealed during the experiments, which have improved the structural and electrical properties, by orders of magnitude. So, the piezoelectric quality of the ZnO film has increased further by the annealing process carried out on our fabricated ZnO films.

5 Conclusion

High-quality ZnO films were fabricated and characterized in this paper. The ZnO film was deposited using dielectric sputtering system under room temperature. AFM showed that the ZnO film has the average grain size around 40.566 nm. The AFM image depicts that the surface of the ZnO film was very uniform, and the surface roughness was 7.882 nm. The rms roughness (*R*q) is 7.882 nm and the difference *R*p–p between the lowest and highest points on the surface is 58.21 nm. Scans over 600×600 nm for thermally annealed sample, were also taken and shown in Fig. 7. In this case, roughness *R*q was found to be 6.56 nm and *R*p–p was found to be 53.54 nm, respectively. Thus, it is concluded for our ZnO samples that as the crystalline size increases, the surface roughness decreases and vice-versa. The SEM cross-sectional image of the ZnO film confirmed that the ZnO film grows columnar, and the direction is perpendicular to the surface. It is observed that, after annealing, the quality of the films is improved by orders of magnitude. After thermal annealing, the average grain size was 50 nm and the improved surface roughness with *R*q measured to be 6.5671 nm with improved current-voltage characteristics and FTIR peak shift of 1 wave number in total. This ZnO film will be used as a piezoelectric layer for fabricating a MEMS actuator.

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Authors' Contributions ASK carried out the preparation of the ZnO films, participated in the characterization of the ZnO films, and drafted the manuscript. PRA conceived the study and participated in its design and experimentation. SD participated in the characterization of the ZnO films and the coordination. All authors read and approved the final manuscript.

Conflict of Interest The authors declare that they have no competing interests.

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