ZnO Thin Film Fabricated by Atomic Layer Deposition: Interplay Between Piezorelectric Response and Film Properties

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Abstract

In this work, zinc oxide (ZnO) thin films were grown on silicon substrate by thermal atomic layer deposition with varying cycle number ranging from 100 to 400. The chemical composition, surface morphology, crystalline structure, electrical and optical properties of ZnO were investigated in terms of their impact on piezoelectric characteristics. We demonstrated that incorporation of hydrogen in the form of Zn-OH bonds and their possible assemblance as ZnO_xH_Y matrix during deposition plays a crucial role in determining not only the composition and features of ZnO thin films, but also sufficiently governs its piezoresponse. It was revealed that the lower the ALD cycle number, the more hydrogen is presented in ZnO, the higher is the donor concentration and the better is the electromechanical response.

Keywords – ZnO, ALD, piezoelectric, hydrogen, photoluminescence

Introduction

Zinc oxide (ZnO), a direct wide bandgap compound, is widely studied and extensively used as a piezoelectric material as in comparison to similar II–VI tetrahedrally bonded wurtzite compound semiconductors it has much better performance [1]. Yet, there is certain gap in knowledge toward full realization of piezoelectric properties of ZnO thin film with thickness below 100 nm as it is hard to achieve fabrication of uniform, pin-hole and surface defect free structure. In this case, atomic layer deposition (ALD) can be considered to be attractive solution as in addition to mentioned characteristics, it also provides tuneable film composition and thickness control at sub-nanometer level [2]. However, not much known in literature about piezoresponse of ZnO fabricated by ALD and especially its correlation with stoichiometry, morphology, optical and electric properties. This work clearly establishes this dependency as it demonstrates that by varying the ALD cycle number, the piezoelectric properties of ZnO could be controllably adjusted.

Experiments

An n-type silicon wafer (100) was used as a substrate material for the deposition of ZnO thin films. The substrate was immersed in a solution of H_2SO_4 and H_2O_2 (ratio 3:1) for 5 min to remove contaminants. The ZnO thin film was deposited on the silicon substrate by ALD. Briefly, the substrate temperature was set at 100 °C and diethyl zinc (DEZ, $(C_2H_5)_2Zn$) and water were used as precursors for zinc and oxygen, respectively. The total number of cycles for the ALD process was 100, 200 and 400 which resulted in naming the samples as ZnO-100, ZnO-200 and ZnO-400, respectively. The crystal structures were analysed by grazing incidence X-ray diffraction (GIXRD, TTRAX III, Rigaku) *via* Cu Kα radiation and an incident angle of 0.5°. The high-resolution X-ray photoelectron spectroscopy (HRXPS) analysis of the samples was access *via* a PHI Quantera AES 650 X-ray photoelectron spectrometer. The piezoelectric force microscopy (PFM)/Kelvin force probe microscopy (KPFM) measure were carried out with Ntegra Aura (NT-MDT) commercial scanning probe microscopes. Photoluminescence (PL) spectra were measured using VUV/UV beamline (TLS-BL03) of a 1.5 GeV synchrotron radiation facility.

Results and Discussion

SEM analysis revealed the formation of uniformly spread particle-based ZnO thin film which dimensions and surface roughness increase following the cycle number. Cross-sectional SEM image determined that ZnO-400 has thickness of ~90 nm which allow roughly estimate ALD growth rate as 0.22 nm/cycle. It is in accordance with literature [2].

XRD analysis demonstrated that all samples have hexagonal wurtzite structure featuring (100), (002) and (101) reflection directions. As positions of these peaks has absence of any shift with varying ALD cycle number, it is concluded that all ZnO thin films has identical lattice parameters. It represents that relative presence of surface defects or incorporated impurities and their influence on

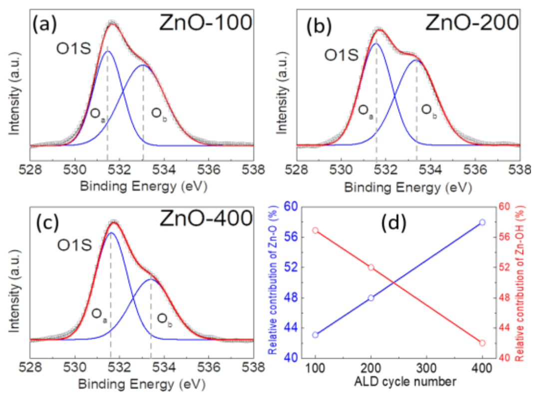

Fig. 1. (a)-(c) O1s XPS bands of ZnO thin films. (d) Linear dependency of presence of Zn-O and Zn-OH bonds in ZnO thin film from cycle number of ALD.

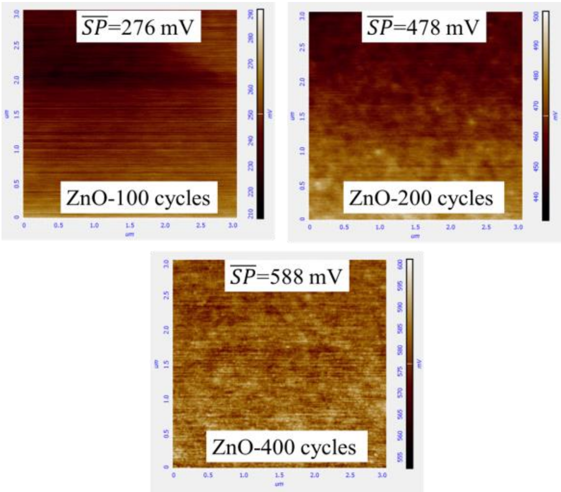

Fig. 2. Surface potential mappings of ZnO thin films.

Furthermore, it is noticed that with higher cycle number, the intensities of reflection peaks increase which represents improved crystallinity as penetration depth of X-rays during analysis is remain the same.

XPS measurements were carried out to determine chemical composition of ZnO thin films. The binding energies of the XPS spectra have been calibrated according to the C1s peak at 284.6 eV. The O1s spectra of ZnO-100, ZnO-200 and ZnO-400 are shown in Fig. 1(a)-(c). For better examination of oxygen chemical states, the O1s bands are deconvoluted into two peaks (O_a and O_b) using Gaussian fitting. The O_a peak located at 531.5 ± 0.2 eV is assigned to the O^{2-} ions surrounded by Zn^{2+} ions in the würtzite structure [3]. The O_b peak at 533.04 ± 0.2 eV is attributed to OH-related bonding [4]. The relative integrated area percentages of the two different oxygen species were calculated from the O1s fitting curves. For ZnO-100, ZnO-200 and ZnO-400, the percentages of O_a and O_b are 43.10% vs. 56.90%, 47.98 vs. 52.02% and 57.96% vs. 42.04%, respectively.

Plotting these values versus ALD cycle number revelated strong linear dependency between thickness of film and presence of both compounds (Fig. 1(d)). As can be seen, the increasing cycle number leads to lowering the presence of unintentionally introduced hydrogen in ZnO which is correlated with its crystallinity.

The delocalized charge transfer was assessed by KPFM since it allows to map surface potential (SP) with precise accuracy (Fig. 2). The average values of SP for the ZnO-100, ZnO-200 and ZnO-400 were determined as ~276 mV, ~478 mV and ~588 mV. It is well accepted that the SP value represents the statistical distribution of electrons quantum states described by the Fermi level, and is proportional to the concentration of donors [5]. Thus, it is clear that with increasing cycle number, the concentration available electrons within ZnO films become lower.

Low temperature ZnO-100 emits an intense UV light by excitation with 200 nm. By contrast, the luminescence is almost quenched in other two samples (Fig. 3). This phenomenon may correlate to the concentration of hydrogen-related impurities and defects in the samples. For the clear explanation of this observation, further analysis of the correlation of the defects to the PL bands are ongoing.

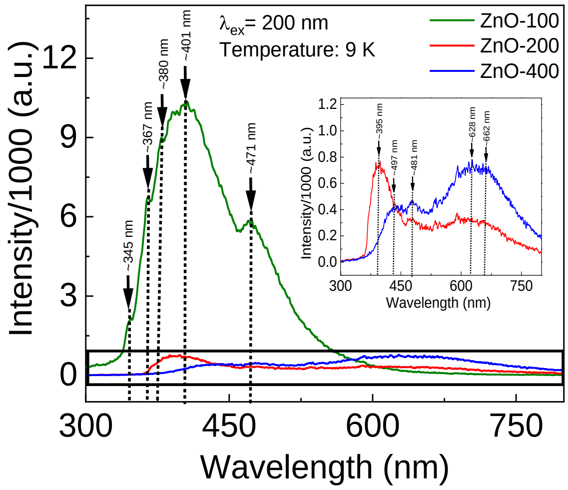

Fig. 3. PL spectra of ZnO thin films.

PFM was utilized to understand how the deposition of ZnO with different ALD cycles number affects its piezoelectric characteristics. Preliminary screening determined that ZnO-100 showed the best electromechanical response followed by ZnO-200 and ZnO-400, consequently. It is interesting to notice that ZnO-400 demonstrated almost complete absence of any ferroelectric-related features which existence is correlated with piezoelectric performance. Detailed investigation and evaluation of this analysis is ongoing.

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