Sputtering of Ga-doped ZnO nanocoatings on silicon for piezoelectric transducers

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Abstract. In this study, lead-free, piezoelectric devices were fabricated by vacuum radiofrequency (RF) sputtering of Ga–doped, ZnO (GZO) nanocoatings at different deposition modes on silicon substrates. Several deposition rates were varied (2 to 16 nm/min) by tuning the sputtering voltage and pressure, in order to control the microstructure and surface morphology of the films. The dependences of the piezoelectric properties of GZO thin films on the different deposition conditions were investigated. Significant dependency of the films’ microstructure and surface roughness was observed to the deposition modes used for fabrication. The results showed that after optimization, the surface roughness of the films grown using sputtering voltage 1.1 kV and Ar=2.5.10^{-2} Torr, is 6 nm. Films with such microstructures are characterized with crystallites orientation (002) and exhibit the highest piezoelectric coefficient of 96.3 pC/m, which is superior compared to other known, lead-free, piezoelectric materials. A simple, membrane–based, vibration sensor was fabricated at the optimal set of conditions to demonstrate the functionality of the coating in a real microelectromechanical (MEMS) device. The working range of the device is between 2 and 800 g and the piezoelectric voltage generated after minimum deformation of 5.4 nm (2g), was 9.66 mV.

1. Introduction
Silicon-based, pressure/vibration sensors have a broad applicability, because of their favorable technological properties, such as ease of control, flexibility by anisotropic etching, lack of mechanical hysteresis and compatibility with the integrated circuits fabrication technology [1]. However, problems with their sensitivity and response time still exist. For this reason, the researchers combined the purely capacitive behavior of such membrane-type, bulk micromachined sensors with piezoelectric response by growing different piezoelectric films (mostly based on lead zirconium titanate - PZT), by variety of methods like sputtering [2], epitaxy [3, 4], pulsed laser deposition, etc. [5]. Recently, material science allowed production of lead-free, piezoelectric materials with high piezoelectric
coefficients, such as Ba$_{1-x}$Ca$_x$Ti$_{1-y}$Zr$_y$O$_3$, (K$_{0.5}$Na$_{0.5}$)NbO$_3$, (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$, ZnO doped by boron (B), gallium (Ga), vanadium (V) and aluminum (Al) [6-9]. The doping approach is applied to increase the conductivity of the piezoelectric films, typically these materials are dielectric in nature, and thus enhance the power produced. The most promising results for achieving controllable and reproducible structures and morphology of the films seem to exist for Ga-doped ZnO. However, the focus of the known studies was on the optical characteristics for application in solar cells and photoluminescent devices (on glass substrates), and less on the piezoelectric response of the films, which require different features of the crystallites as compared to these necessary for the optoelectronic elements [10,11].

In this paper silicon wafer with crystallography orientation (100) was used as a substrate and ZnO was co-sputtered with Ga by RF sputtering for films with different thicknesses, produced at different growth rates. Analysis of the samples by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) gave information about the dependences of the structural, elemental and morphological properties of the GZO thin films at different deposition conditions on the piezoelectric behavior and sensing properties.

2. Experimental section

In this study, radio frequency (RF) (13.56 MHz) sputtering was applied to deposit the GZO thin films. ZnO (50 wt %) and Ga (50 wt %) were compounded in target with a 3 inch diameter. The area of the Si (100) substrate was about 3 cm x 3 cm. The substrates were preliminary cleaned in hydrofluoric acid to strip the native oxide film on the top of silicon. The chamber was evacuated to vacuum level of $10^{-5}$ Torr, and then the deposition parameters were controlled at pressures between $10^{-4}$ Torr and $10^{-1}$ Torr and voltages between 0.7 kV and 1.3 kV (plasma power in the range 35 W-234 W) in order to achieve different crystalline parameters and films compositions. Two different growth times were set for each combination of deposition modes to produce different films thicknesses. The thicknesses of the GZO thin films were measured using a-step Tencor profiler. The deposition rate was between 2 and 16 nm/min and it was calculated based on averaging 3 samples thickness measurements data. The roughness (or flatness) was monitored using atomic force microscopy (AFM) MFP-3D, Asylum Research, Oxford Instruments in non-contact mode, and the crystalline structure was investigated using Philips PW-1724 X-ray diffraction (XRD) patterns with CuKα radiation. The surface chemical composition and bonding of the GZO thin films were analyzed using the X-ray photoelectron spectrooscope (XPS) ULVAC-PHI 5000. Piezoelectric coefficients were calculated based on capacitance and voltage generated measurements, following standard charge excitation procedure, described elsewhere [12]. Capacitance was measured by LCR-819 - GW Instek RLC Impedance meter and the shape of the voltage generated was recorded with digital oscilloscope DQ2042CN. The test setup for the piezoelectric coefficient was chosen, considering elasticity coefficient of the additional vibration system. It was proven that in this way the width of the frequency range at constant vibration could be broaden, as well as the amount of generated charge is greater [13]. The simple, membrane-based, sensing structure was obtained following standard bulk micromachining procedure (thermal oxidation of silicon – photolithography patterning of SiO$_2$ – wet anisotropy etching of uncoated with SiO$_2$ wafer in 40% KOH solution at 30°C). For the sensor device, back side and top membrane electrodes were produced by thermal evaporation of aluminum (240 nm). Intermediate piezoelectric film was grown by using the optimal deposition parameters, namely plasma power of 136 W and working pressure of $2.5.10^{-3}$ Torr, because the deposited GZO thin films had the most uniform and regular surface, and acceptable growth rate. Sensor element loading ability and working range was detected by laboratory-made testers for dynamic loading with variable magnitude and frequency of the vibrations generated.
3. Results and discussion
As figure 1 shows, the films deposited at different sputtering voltage showed different peak intensities (002), typically appearing between 28° and 35° depending on the substrate used and film thickness. These results suggest that the Ga-doped ZnO thin films deposited at higher plasma power, hence higher temperatures, have a stronger asymmetry in the crystalline structure. The rest of the peaks are suppressed in the range 2θ = ~ 50-60°.

![Figure 1. XRD patterns of Ga-doped ZnO thin films on silicon as a function of the deposition voltage and pressure.](image)

The grown films exhibited surface states with increasing average roughness when the sputtering voltage and pressure increased, as shown in the AFM 3D topographies (figure 2).

![Figure 2. AFM images of the Ga-doped ZnO nanocoatings sputtered on silicon wafers at different conditions.](image)
18 nm roughness was observed for film thickness of 194 nm, grown at sputtering voltage of 1.3 kV and pressure \( \text{Ar} = 2 \times 10^{-2} \) Torr. The coating, grown at 0.7 kV and \( \text{Ar} = 2 \times 10^{-2} \) Torr shows high roughness of almost 14 nm. It is in contrast to the normal trend that at low deposition rates the films consist of small, uniform in size grains. Similar inconsistence is reported by Qui et al. [14] for evaporated film produced of low density vapor flux. By similarity, the possible reason for this reverse behavior at the lowest sputtering voltage is the insufficient energy of the particles, forming columnar grains and voids between them without possibility for particle diffusion and homogenization. Increasing the sputtering pressure at constant voltage results in decrease of the mean free path of the particles and due to overcrowding in the gap of the vacuum deposition chamber, the roughness also increased. It could be seen that rms roughness can reach 21 nm for film with thickness of 216 nm at \( \text{Ar} = 6 \times 10^{-4} \) Torr and \( U = 1.1 \) kV. Acceptable surface roughness of \( \sim 6 \) nm, considering reliable contact with the next electrode film, exhibited the coatings produced at 0.9 kV and 1.1 kV at \( \text{Ar} = 2 \times 10^{-2} \) Torr, which is in agreement with the results in [15]. From both layers, the XRD results showed better crystallinity for those, grown at 1.1 kV revealing four additional peaks in its diffractogram between 33° and 36.24° that could be ascribed to the substance under study (figure 3 up). This is the reason to select these particular deposition conditions for the further simple sensor element design. To completely investigate the relationship between the deposition conditions and chemical composition, the chemical structure of Ga-doped ZnO thin film at the optimum deposition conditions was investigated by XPS (figure 3 down).

![XRD diagram](image)

**Figure 3.** XRD of selected film grown at optimal deposition conditions (up) and XPS spectroscopy of the same film (down).

The measurement showed that no apparent peak is observed in the spectra of the Ga and ZnO constituents of the film, which suggest that binding state of new formation of \( \text{Ga}_2\text{O}_3 \) appears and starts dominating. Similar results are reported, where GZO films are sputtered on glass [15]. This could be a possible reason for enhancement of the piezoelectric properties. Different bond existence was detected by the spectrophotometer for Ga-doped ZnO thin films deposited on silicon (100) substrates, as can be
seen from XPS spectrum (figure 3 down). The state corresponding to the O1s spectrum was divided into three components, centered in the range ~530 eV-533 eV for all characteristic peaks. The peak with higher binding energy is associated with O²⁻ ions in oxygen vacancies within substrates that have poor crystallization, as the figure shows. Based on the results, it can be concluded that there are more oxygen vacancies existing in GZO thin films. Regarding the low-energy peak, it was due to poor adhesive strength of Ga-doped ZnO thin films to the silicon wafer. Decrease of oxygen vacancies and the increase of oxygen absorption, may improve the piezoelectric properties of the films [16,17].

Piezoelectric coefficients were obtained, following the measurement procedure validated for silicon cantilever with defined geometry and size [18]. The cantilever was fixed at one of the ends, while the opposite side was free standing. By supplying vibration with certain frequency (related to \( \omega \)) and magnitude (A), producing deflection and due to suitable electrode patterning and placement, it was possible to determine the transvers piezoelectric coefficient \( d_{33} \) (equation 1). In this way, the measured voltage from peak to peak \( (U_{p-p}) \) is related to the strain applied, the area activated between the electrodes, resonant frequency of the beam, due to its geometry and some parameters of the measurement equipment (resistance and capacitance R and C of the oscilloscope).

\[
U_{p-p} = \frac{A.S.e_{33}}{C} \cdot \frac{R^2C^2\omega^2}{1 + R^2C^2\omega^2 [1 + \exp \frac{-t}{RC}]} \quad [18]
\]

The formula was used to determine the electrical displacement coefficients \( e_{33} \). They are related with the piezoelectric coefficients through the elastic compliances for stress under steady electric field (in reverse direction to the Young’s modulus). This method is simple, reliable, provides high resolution and accuracy better than ± 0.5 pC/N [19]. The data obtained after this measurement for films, grown at different sputtering voltages and pressures, as a function of the vibration frequency are shown in figure 4.

![Figure 4](image-url)

**Figure 4.** a) Piezoelectric coefficient \( d_{33} \) as a function of the vibration frequency for GZO sputtered at: a) 0.9 kV and 1.1 kV (constant pressure of 2.5x10⁻² Torr); b) 9.10⁻⁴ Torr and 6.10⁻¹ Torr (at constant sputtering voltage of 1.1 kV).

The results show enhanced conversion efficiency of the coating at lower frequencies with maximum at 16-17 Hz, respectively, depending on the deposition parameter and decreasing with further increase of the frequency. Overall, the results suggest that the modification of the deposition mode by increasing the sputtering voltage, results in enhancement of the asymmetry of the crystal lattice, as it can be seen from the XRD measurements. Although irregularities on the surface still exist, it was possible to enhance the piezoelectric behavior of Ga-doped ZnO nanocoatings. On the contrary, the increase of the sputtering pressure resulted in degradation of the properties. Two basic factors, i.e. the irregularities and crystallinity of the material, have contributed to the variation of the piezoelectric coefficients. Grain boundaries are considered as non-polar type traps for the charge carriers, therefore, films, deposited at voltage higher than 0.8 kV, which are characterized with larger grains, have affinity
to generate greater piezoelectric response due to the lower number of such boundaries. The behavior is similar at higher argon partial pressure. Such relations have been reported in [20] for piezoelectric ceramic with ZnO content. The observed peaks in the 3D AFM scanned images, contributed to the formation of defects, influencing the domain zones uniformity and inducing polarization quenching, which results in the weaker piezoelectric properties [21].

In order to estimate the sensing characteristic, membrane-based, vibration sensor was fabricated using Ga-doped ZnO film that exhibit maximal piezoelectric coefficient (figure 5).

![Figure 5](image)

**Figure 5.** a) Multiple membranes, bulk micromachined in silicon (100); b) single membrane, scribed and separated from the wafer having coated inner part with piezoelectric – face side; c) cross-sectional view of piezoelectric coated silicon micromembrane.

The backside was coated with patterned aluminum electrode. The element was tested at constant frequency of 16 Hz and varying vibration strength, creating in this way mechanical load in the range of 2 – 800 g. Due to the excellent mechanical properties of the silicon membrane without hysteresis, the output voltage, generated under strong wave, was tested at high load up to 800 g. The sensing element worked properly, without damage, even just before the strongest excitation and then breaks.

![Figure 6](image)

**Figure 6.** a) Voltage vs time (oscilloscope view) for cyclic repeating compression – tension of the structure at relatively low load of 2 g, demonstrating the sensor sensitivity; b) voltage versus load weight in the range of 2-800 g.

Figure 6a shows the variation of the output voltage with the time under cyclic loading with repeated pressure and tension with the sinusoidal excitation wave, equivalent to load of 2 g. Figure 6b shows the effective (rms) value of the piezoelectric voltage, produced during the membrane deflection. Although the linear response of the sensor, the signal should be further filtered by a high-order filter with enhanced selectivity and frequency tuning [22]. Nevertheless, at minimum film deformation of 5.4 nm, calculated according to Hook’s law [23], the piezoelectric voltage was 9.66 mV. After applying greater load than 800 g, the membrane started tearing apart and the signal is abruptly interrupted, therefore the limiting factor in this case is not related to the GZO films capabilities. By the
best of the author knowledge, the results are superior as compared to the sensor response of similar constructive design, but using different lead-free materials.

4. Conclusions
In this study, nanosized films of Ga-doped ZnO were successfully RF sputtered on silicon wafer with crystallographic orientation (100) suitable for bulk micromachining and membrane-based sensor fabrication. It was found that film with rms roughness ~6 nm (thickness ~103 nm) and dominant orientation of crystallites (002) grown at sputtering voltage 1.1 kV and Ar=2.10⁻² Torr, exhibited the highest piezoelectric coefficient of 96.3 pC/m for single frequency of 16 Hz. The sensor was tested at loading at this frequency and different vibration strengths whilst the piezoelectric response was analyzed. The sensor is characterized by high sensitivity and broad operational range, as compared to similar sensors using other lead-free piezoelectric materials, due to the optimized sputtering conditions of GZO films. Future work will be related to filtration of the produced signal and study of the pyroelectric behavior of this material for fabricating multifunctional sensor “2 in 1”, detecting pyro- and piezoelectric effect simultaneously for variety of transducers and energy harvesting applications.

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