Electrical and Microstructural Characterization of TiO₂ Thin Films for Flexoelectric Devices

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Abstract. This work investigates the flexoelectric potential of titanium oxide thin films regarding their microstructural and electrical properties to be integrated into nanoscaled resonators. Flexoelectricity is an electromechanical effect that can result in deformation of a material due to a polarization gradient and can outperform piezoelectric effects at the nanoscale. The flexoelectric constant is linearly dependent on the permittivity and therefore we determined TiO₂ as a suitable flexoelectric material because of its high permittivity, its CMOS compatibility and its linearity with respect to polarization. TiO₂ capacitors with various electrode materials are evaluated in order to achieve the c-axis oriented (110) rutile growth, thus to exploit the highest permittivity. The permittivity ranges from 65 to 95, with TiO₂ on IrO₂ electrodes representing the highest value achieved in this study. As expected, the IrO₂/TiO₂/IrO₂ capacitors show an almost constant impedance up to 200 kHz and have leakage current density values of ~10⁻³ A/cm² at 0.5 MV/cm at room temperature.

1. Introduction

The flexoelectric effect describes the relationship between the strain gradient and the polarization developing thereof. The converse effect is mechanical strain generated by a polarization gradient. Compared to the piezoelectric effect, which links mechanical strain generated by polarization, the flexoelectric effect is independent of the crystal symmetry and scales with the inverse of the thickness. For a non-piezoelectric material, the constitutive equation for the converse effect is given as [1]:

\[ \sigma_{ij} = c_{ijkl}u_{kl} + f_{ijkl} \frac{\partial P_k}{\partial x_l} \] (1)

where \( \sigma \) is the stress tensor, \( P \) is the polarization, \( c \) is the elasticity module, \( f \) is the flexoelectric coupling constant, \( u \) is the strain and \( x \) are the spatial coordinates in \( l \) direction. In this equation, the Einstein notation is used. This strain generating effect can be used in a variety of ways, for example to excite a resonator, which can then be used to measure viscosity of liquids or particle mass [2].

A straightforward resonator design consists of a cantilever as key component, whose realization is well-established in silicon MEMS (micro electromechanical system). A basic schematic is shown in figure 1. Basically, it is a free-standing capacitor which is clamped on one side, so that the beam can resonate when a force based e.g. on the flexoelectric effect is applied. Even though at first sight a flexoelectric
cantilever cannot work, as the polarization gradient in a capacitor should be zero, it was early shown, that flexoelectric bending of a cantilever can occur [3]. The reason is that at the interface the polarization does not instantly drop to zero, but continuously declines. The bending that occurs is then mostly dependent on the flexural rigidity of the cantilever which is thickness dependent, the flexoelectric constant and the applied electric field, respectively.

Figure 1 Schematic cross-sectional view on a flexoelectric cantilever. If an electric potential difference is applied between both electrodes, a polarization curve, as depicted next to the cantilever, develops.

The flexoelectric effect gained a lot of interest in the last decade. As MEMS devices get smaller and smaller, the flexoelectric effect becomes a dominating electromechanical effect in dielectric materials and needs to be considered even for piezoelectric devices. At scales in the nanometre range (~100 nm and below), flexoelectric actuation can dominate in common piezoelectric materials like lead zirconium titanate or zinc oxide [4]. Within CMOS; titanium dioxide is a promising material for flexoelectric applications, as the flexoelectric constant scales with the permittivity of a material and TiO$_2$ has a very high permittivity of up to 200 for c-axis oriented single crystals. The permittivity of a material mainly is directly related to the crystal structure, therefore an investigation of the microstructure of the material is necessary. The crystal quality, in turn, depends on a lot of parameters, such as the growth method and the substrate properties. Both have a strong influence how the atoms can arrange themselves in a lattice. The growth method determines the surface mobility of the adatoms and the substrate provides the crystallographic information to the growing films. We choose sputtering as the deposition technique as the adatom mobility can be high and it is a technique offering a high deposition rate and is well established in industry. In our case the properties of the TiO$_2$ will will be strongly influence by the bottom electrode.

It is the objective of this work to determine the influence of selected bottom electrode materials for a flexoelectric resonator and characterize the microstructure and the electrical properties of sputter-deposited TiO$_2$ thin films.

2. Methods and Experimental Details

For the microstructural and electrical characterization of the TiO$_2$ layers metal-oxide-metal capacitors with various electrode metals were realized, whereas the top and bottom electrode always consists of the same material. As substrate we used standard 4 inch n-doped silicon wafers with a bulk resistivity of ~50 $\Omega \cdot \text{cm}$. To start, the wafer was first dipped in hydrofluoric acid to remove the native oxide. Then the bottom electrode was deposited by sputtering or thermal evaporation. The electrode materials investigated in this study were platinum, gold, iridium and iridium dioxide. We carefully selected these metals because we want to avoid any oxidation that might affect the metal-TiO$_2$ interfaces, which can have an impact on the permittivity. The platinum and iridium electrode were sputtered at 500 W from a 4 inch target in a 6 µbar argon atmosphere. The distance of the electrodes was 65 mm. The iridium oxide electrode was reactively sputtered at 500 W at a back pressure of 2 µbar in a pure O$_2$ atmosphere. The gold electrode was deposited by thermal evaporation. Subsequently, the titanium dioxide was reactively sputtered at 800 W from a 6 inch target at 2 bar again in a pure O$_2$ atmosphere. For the realization of the
The top electrode a lift-off method was used. The top electrodes were either circular or square-shaped pads. The thickness of the TiO$_2$ is about 100 nm and the electrodes are about 200 nm thin each. The crystallographic phase composition was determined with X-ray diffraction measurements in Bragg-Brentano configuration. The capacitance was determined by measuring the impedance with a Hioki IM3533-01 LCR-Meter. A 2-point measurement approach was used and based on a straightforward capacitor-resistor equivalent circuit the capacitance was calculated. The leakage current was measured at room temperature with a Keysight B2900 precision source/measure unit.

3. Microstructure of TiO$_2$ Grown on Different Electrode Materials

Basically, titanium dioxide has three common crystallographic phases: rutile, anatase and brookite. Rutile represents the most stable microstructure [5]. Anatase is a metastable phase, which converts to rutile at higher temperatures (above 500°C) [5]. Brookite is the rarest of the crystal structures as it is only stable under very specific conditions and thus, is of no importance to this study. For flexoelectric applications, rutile is the preferred phase, as it has a higher permittivity (> 90) compared to anatase (< 40), so that a higher flexoelectric constant is expected. The permittivity is anisotropic in this material and depends on the crystallographic direction. As the c-axis orientation has a higher permittivity than any other direction, a growth in the (110) direction indicating the c-axis is preferred [6]. The impact of different electrode materials was studied, since the electrode material determines not only the electrical properties of the complete capacitor due to the barrier that forms at the interface, but also influences the microstructure and the quality of the TiO$_2$ layer. Figure 2 shows the XRD characteristics of the samples realized with different electrode materials. When applying iridium as electrode material, the TiO$_2$ is only in the rutile phase, but features a poor peak characteristics. The iridium oxide electrodes on the other hand show a significant increase in the peak height. The favorable growth on the iridium dioxide can be attributed to the excellent match of the rutile IrO$_2$ and the rutile TiO$_2$ phase with respect to lattice structure and lattice constant. When choosing this electrode material and the sputter deposition parameters, given above, no anatase-related peaks are detected. When starting with platinum (Pt) both the rutile and the anatase phase are detected, whereas the latter is unwanted for our high-k application. The presence of the anatase phase on Pt electrodes is also in accordance with results reported in other studies [7]. On the gold electrodes, however, the TiO$_2$ is almost amorphous, indicated by a low and wide peak for the rutile phase.
4. Permittivity of the different electrodes

As the permittivity is a key parameter in the flexoelectric-related figure of merit [1], this important material parameter of TiO$_2$ was measured and evaluated on different electrodes. The corresponding measurements were made with test capacitors having varying top electrode sizes ranging from 0.0025 mm$^2$ to 0.8 mm$^2$. When applying the basic formula for planar capacitors, Figure 3 shows the capacitance-thickness product as a function of the top electrode area times the vacuum permittivity for different electrode materials, so that the slope of the curve is equal to the relative permittivity. Figure 3(a) shows the curves for iridium, iridium dioxide and platinum. The design for the top electrode of gold was different, with much larger areas and can be seen in figure 3(b). The standard electrode materials, gold and platinum, have the worst performance with respect to the permittivity, resulting in a value of about 65. For the platinum it is clear that the anatase phase lowers the permittivity. In case of the gold electrode, the poor crystallinity is probably the cause for the low permittivity of the TiO$_2$ layer. Since the TiO$_2$ on the gold and the iridium electrodes shows the same crystal structure it is unclear why the TiO$_2$ on iridium shows a higher permittivity. The results for the iridium and iridium oxide are comparable to the work of Joo et al. [8], who also investigated the difference of the electrical properties of TiO$_2$ on iridium or iridium oxide electrodes. As our results show, iridium oxide is the optimal choice as an electrode material. The permittivity values of TiO$_2$ on IrO$_2$ are also among the highest for sputtered TiO$_2$ films (i.e. 50-70 compared to 95 in this study) [9-11]. Therefore, for our following studies we focus on the characterization of an IrO$_2$/TiO$_2$/IrO$_2$ capacitor.
5. Capacitance and Leakage Currents of an IrO₂/TiO₂/IrO₂ Capacitor

The characterization of the MIM capacitors focused mainly on the frequency dependent capacitance and the DC leakage current behaviour. An LCR meter measures the real (X) and imaginary (R) part of the impedance \( Z = R + iX \). According to the equivalent circuit of a capacitor parallel to a resistor the calculation for the loss angle \( \theta \) is shown in the following formula:

\[
\tan(\theta) = \frac{X}{R} = \frac{1}{\omega C_p R_p}.
\]

Here, \( \omega \) is the angular frequency, \( R_p \) the parallel resistance and \( C_p \) the parallel capacitance. In figure 4 frequency dependency of the (a) capacitance and the loss angle for different electrode areas are shown. The capacitance density \( C_p/A \) shows no dependence of the frequency and the electrode area. In this figure the loss angle is also shown. In an ideal capacitor the current should lag behind the voltage by -90°. The values are with -88° close to -90° at lower frequencies and drop to -80° at higher frequencies. For the smaller pads the loss angle is constant at lower frequencies and drops slightly at higher frequencies. This is an expected behaviour, as at low frequencies the imaginary part of the impedance of a capacitance \( 1/\omega C \) is very high and is the dominating term. At higher frequencies, however, the resistance of the capacitance decreases and the resistance which does not induce a phase shift, becomes dominating, explaining the change in the phase. For bigger capacitors the decrease in the loss angle is stronger and the capacitance drops. One explanation of the decrease in capacitance is, that the leakage currents of the TiO₂ capacitor is too high at the larger electrode areas (i.e. 500²µm²). A high leakage current can interfere with the impedance measurement.

The leakage current density over the applied electric field of a circular capacitor with 500 µm in diameter is given in figure 4 (b). In practical applications the deposited TiO₂ is never fully stoichiometric, having a low percentage of missing oxygen [12]. There are two main defects in the material, namely titanium interstitials and oxygen vacancies and both contribute to the leakage current behaviour. Based on these structural defects, the dominating leakage current mechanisms of a TiO₂ capacitor are related to Poole-Frenkel- and trap-assisted-tunnelling effect [13]. Typically, with Poole-Frenkel, effects are summarized, where crystal defects, such as substitutional atoms, interstitials, vacancies or Frenkel pairs cause the existence of higher energy states, called traps. Electrons in these traps need less thermal energy to get into the conduction band. Trap assisted tunnelling is an effect similar to Poole-Frenkel with the difference being, that the electrons can escape a trap by tunnelling.
either directly into the conduction band or to other traps. In addition to these leakage mechanisms it was recently shown, that TiO₂ also forms conductive paths through individual grains [13]. These conductive grains have been shown to have a rectifying behaviour for Pt/SrTiO₃/Pt capacitors. This mechanism could also explain the slight rectifying behaviour of our TiO₂ capacitor, which can be seen in figure 4 (b). In comparison to the work of Jithin et al. where sputtered TiO₂/RuO₂/TiO₂/RuO₂ capacitors are investigated [14], the capacitor of this study offers a lower leakage current densities of about 3 magnitudes. Compared to the works of Racko et al. [15] and Fröhlich et al. [16], where the TiO₂ was deposited by atomic layer deposition, the present capacitor shows similar leakage current levels.

6. Conclusion

The flexoelectric effect is an important electromechanical property of dielectrics, which can have a higher actuation potential than piezoelectric materials at nanoscale applications and need to be considered in piezoelectric NEMS devices. Due to its high permittivity, titanium dioxide is a very promising candidate for flexoelectric applications. We produced sputtered TiO₂ test capacitors with varying electrode materials and determined the phase composition and the permittivity. Next, we measured the spectral response of the impedance and the leakage current of a state-of-the-art full oxide capacitor with iridium dioxide as the electrode material. The results show high values of the permittivity ~95 and leakage current densities of 10⁻³ A/cm² at 0,5 MV/cm, which is among the best performances for sputtered TiO₂ capacitors.
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