PREPARATION OF [001] ORIENTED TITANIUM THIN FILM FOR MEMS APPLICATIONS BY KAUFMAN ION-BEAM SOURCE

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Abstract

We propose the sputtering deposition providing titanium thin films with controlled properties such as preferential crystallography and residual stress using Kaufman ion-beam source. The titanium thin films with thickness of ≈ 80 nm were deposited on [001] Si wafer covered by SiO_2 deposited by plasma-enhanced chemical vapor deposition. To achieve the required crystallography and stress properties, we investigated the different beam voltage of Kaufman ion-beam source and controlled the substrate temperature during deposition using a built-in heater. We used two X-ray diffraction methods to determine the planes parallel to the sample surface and residual stress. We also measured the current-voltage curves to determine the resistivity (ρ) and the thermal coefficient of resistivity (α) of titanium thin films at different substrate temperatures using 4-probe measurement setup. We showed that it is possible to prepare stress-free titanium thin films with pure [001] orientation at the lowest beam voltage of 200 V and substrate temperature of ≈ 273 °C. The corresponding lattice parameters a_0 and c_0 were (2.954 ± 0.003) Å and (4.695 ± 0.001) Å, respectively. Electrical parameters of this sample as ρ and α were $(9.2 \pm 0.1)\cdot 10^{-7}$ Ω·m and $(2.6 \pm 0.2)\cdot 10^{-3}$ K^{-1}, respectively. We found out that these layers are well suitable for micro-electro-mechanical systems where the pure [001] orientation, no residual stress and low ρ and high α are essential. We found that ρ and α are dependent on each other. The ρ value was ≈ 2× higher than the bulk material value, which is an excellent result for a thin film with the thickness of ≈ 80 nm.

Keywords: Titanium thin film, [001] orientation, stress-free, thermal coefficient of resistivity, resistivity

1. INTRODUCTION

Titanium is a commonly used material in microelectronics, microelectromechanical systems (MEMS) or microfluidic systems due to its low value of electrical resistivity of $4.2\cdot 10^{-7}$ Ω·m. It also possesses an extraordinary chemical resistance, an excellent thermal stability, high melting temperature of 1668 °C, high hardness, and a very low number of crystallographic imperfections [1-5].

Titanium belongs to a group of biocompatible materials and is also compatible with the complementary-metal-oxide-semiconductor (CMOS) processes; thus, it is commonly used for device fabrication using lines dedicated to CMOS production and research [6]. In a thin film format it is used in MEMS devices such as infrared bolometers [7], flexible and wearable heartbeat sensors [8], cochlear implants [9], piezoelectric resonators [3], piezoelectric energy harvesters [10], and microfluidic devices [11].

Titanium thin films are typically deposited by the physical vapor deposition (PVD) methods including thermal and electron beam evaporation, pulsed laser deposition, or sputtering, either magnetron or ion-beam based. Different deposition parameters and techniques result in various film properties such as crystallographic parameters, roughness, residual stress, electrical sheet resistance, and thermal coefficient of resistance [12].

Layers used in MEMS technologies are typically required to have minimal residual stress as this significantly affects the mechanical [13] and electrical [14] properties of the final device because the excessive stress level can negatively affect the device performance and even cause damage to its structural integrity [15]. The crystallographic orientation of thin titanium thin films is also crucial for properties of consequently deposited piezoelectric layers such as AlN [16].

Here, we report on a deposition of stress-free highly [001] oriented titanium thin film growth on SiO_2 using a 3-grid radio frequency inductive coupled plasma (RFICP) Kaufman ion-beam source. The most important advantage of the Kaufman ion-beam source is a well-defined process control. To achieve the required crystallography and stress properties, we investigated the different beam voltage of Kaufman ion-beam source and controlled the substrate temperature during deposition using a built-in heater. In our work, we concentrated on the investigation of the control of residual stress by the substrate temperature (T) and its influence on properties of titanium thin films especially on their preferential crystallographic orientation, resistivity (ρ) and thermal coefficient of resistivity (α).

2. EXPERIMENTAL PART

2.1. Deposition process

We deposited the (80 ± 1) nm thick Ti thin film on substrates (20 × 20) mm. The substrates were cut out of p-type Si wafers with diameter of ≈ 100 mm, crystallographic orientation of [100], thickness of ≈ 375 µm, and specific resistivity in the range from ≈ 6 Ω·cm to ≈ 12 Ω·cm covered with SiO_2 layer deposited by plasma-enhanced chemical vapor deposition with a thickness of ≈ 200 nm. The Ti thickness was monitored by calibrated quartz crystal microbalance method during deposition process.

The Ti layers were deposited by the RFICP Kaufman ion-beam source (Kaufman & Robinson - KRI®) with an ≈ 4 cm diameter Mo 3-grid dished focused ion optics with an ≈ 45° ellipse pattern. We used an Ar ion-beam with purity of 99.99999% to provide the bombardment of a ≈ 100 mm × ≈ 100 mm Ti target with the purity of 99.995% under an incidence angle of ≈45°. Ion-beam space charge was reduced by KRI LFN 2000 charge neutralizer (KRI®). The vacuum chamber was evacuated to the pressure of $\approx 5 \cdot 10^{-7}$ Pa before each deposition process. To reach the required thin film parameters, we published earlier, we changed the beam voltage (BV) in the range from 200 V to 1200 V [17] and T was changed in the range from ≈ 105 °C to ≈ 295 °C [18].

2.2. Beam voltage and temperature influence

In the first series of experiment, we changed the BV value in the range from 200 V to 1200 V at the constant temperature of ≈ 105 °C which is given by the flux of deposited material. In the second series of experiment, the T was changed in the range from ≈ 105 °C to ≈ 295 °C with constant ion-beam source BV determined from the first series of experiment. Other corresponding parameters such as acceleration voltage, beam current, radio frequency power, Ar gas flow, and space charge neutralization were set according to the KRI® datasheet recommendations [19]. In the second series of experiment, we changed the T in the range from ≈ 105 °C to ≈ 295 °C.

We used XRD in the Bragg-Brentano (BB) setup with the 2θ angle ranging from 30° to 90° to perform the phase analysis of all Ti thin films. The interval from 60° to 78° was excluded to avoid the high intensity of Si 400 diffraction in this range. We detected diffraction peaks belonging to [100], [101] and [001] crystallographic planes. For [001] crystallographic plane, second order diffraction 002 and fourth order diffraction 004 were measured since the first order diffraction is forbidden. The corresponding X-ray diffractograms for different BV and for different *T* are showed in **Figure 1A** and **Figure 1B**, respectively.

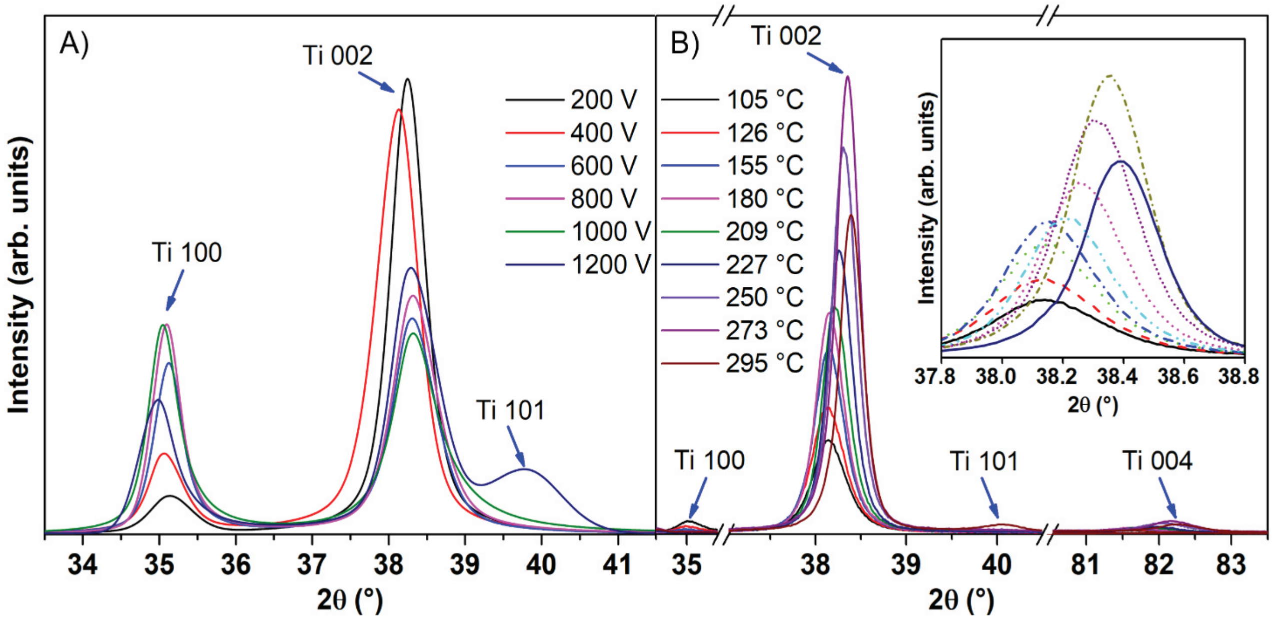

Figure 1 X-ray diffractograms in BB setup of deposited Ti thin films showing the influence: A) of different BV in the range from 200 V to 1200 V at constant *T* of ≈ 105 °C; B) different *T* in the range from ≈ 105 °C to ≈ 295 °C at constant BV of 200 V. The range from 60° to 78° was excluded due to Si 400 diffraction with intensity of several orders of magnitude higher than of the Ti diffraction peaks

The obtained results for different BV (**Figure 1A**) show that there are changes in crystallography of deposited layers. In case of low BV of 200 V and 400 V, we achieved [001] preferential crystallographic orientation with small contribution of [100] planes parallel to the sample surface. On the other hand, the (100) contribution raised with higher BV, mainly in the range from 600 V to 1000 V. We also detected the small contribution of [101] plane orientation along with the [100] and [001] ones for the sample prepared at the highest BV of 1200 V.

Since the sample prepared at the lowest BV of 200 V had the [001] preferential orientation with the smallest compound of [100] orientation, we fixed this BV value and other ion-beam source parameters and changed the *T* (**Figure 1B**). The *T* has influence on peak shift, which corresponds, to residual-stress in thin film, which is described in the next chapter. We also found out that the increasing *T* towards to ≈ 273 °C has positive influence on X-ray diffraction intensity, [100] plane removing and peaks have lower full width at half maximum (FWHM). Only the sample prepared at ≈ 295 °C has higher FWHM and there was detected the small compound of [101] plane parallel to the sample surface. The FWHM value of stress-free sample was ≈ 0.27 °.

2.3. Determination of residual stress

We measured the residual stress σ_f as substrate curvature (**Figure 2A**) and we also calculated the in-plane σ_{xx} and the out-of-plane σ_{zz} residual stress (**Figure 2A**) using the determined lattice parameters from peak position (**Figure 2B**). In-plane lattice parameters *a* were determined from measurement using parallel beam setup and the out-of-plane lattice parameters *c* were determined from measurement in BB setup (**Figure 1B**). We presented this method for residual stress characterization earlier [18].

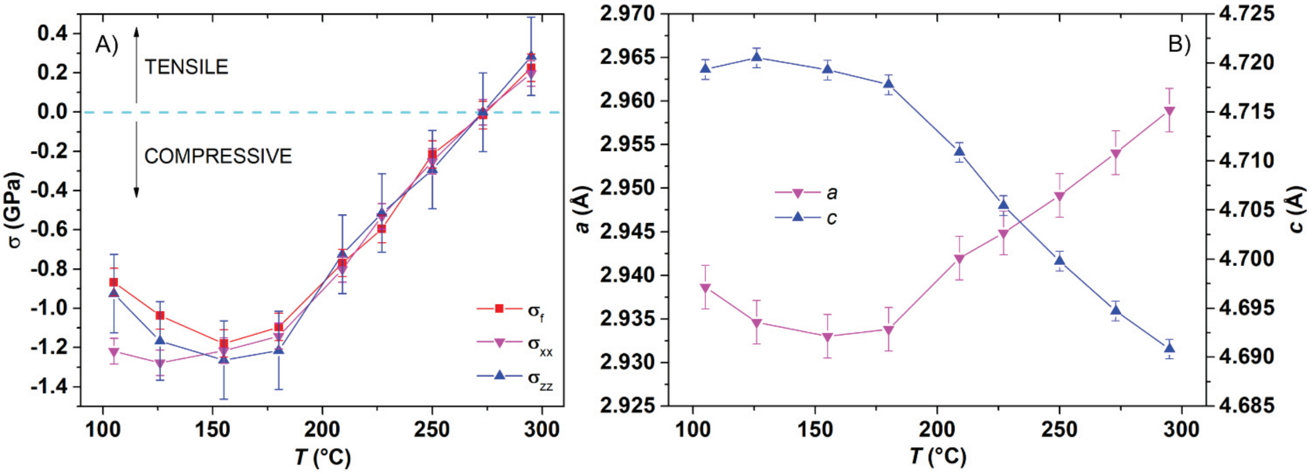

Figure 2 A) Stress dependence of measured σ_f and calculated σ_{xx}, σ_{zz}, values on *T*;
B) Dependence of measured *a* and *c* of deposited Ti thin films on *T*

We found out that the Ti thin film deposited at BV = 200 V and *T* ≈ 273 °C has the zero residual σ_f value within the experimental precision of ≈ 0.1 GPa with the corresponding $a_0 = (2.954 \pm 0.003)$ and $c_0 = (4.695 \pm 0.001)$ Å. From the **Figure 2A** is obvious that the calculated values of σ_{xx} and σ_{zz} are in good agreement with measured σ_f determined from independent curvature measurement. The compressive residual stress is reduced with increasing *T* towards to tensile stress reached for the sample prepared at the highest *T* of ≈ 295 °C. Only first and second sample have lower compressive stress then next one which could be due to different ratio of impurities which were not removed at low *T* [20].

2.4. Determination of electrical conductivity and thermal coefficient of resistivity

In case of demanded applications, we determined α and ρ to prove if the Ti thin films are useful for MEMS applications, where these electrical parameters are important for correct functionality. Both parameters were determined from measurement based on 4-probe method. We measured all samples 5× to get more accurate values. We determined the ρ from current-voltage curves, which were measured in the range from -0.5 V to 0.5 V at constant temperature of ≈ 22 °C. The α parameter was additionally extracted as slope of resistivity dependent on sample temperature in the range from ≈ 25 °C to ≈ 110 °C.

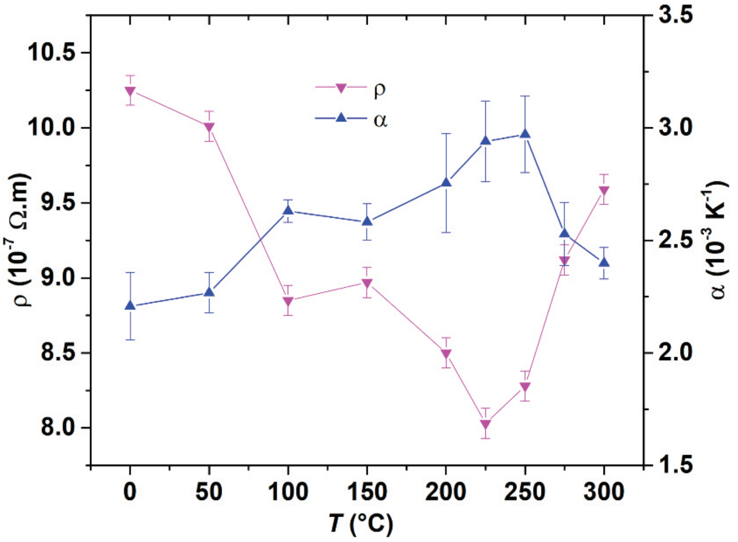

Figure 3 Determined values of α and ρ based on different *T* in the range from ≈ 105 °C to ≈ 295 °C at constant BV of 200 V

Figure 3 shows that there is certain dependence of ρ and α parameters on temperature. Although, the XPS did not show different results for all samples, this could be probably influenced by certain amount of impurities in Ti thin films, as it is excellent getter material. Measured values of the ρ were in the range from ≈ $8.0 \cdot 10^{-7}$ Ω·m to ≈ $10.2 \cdot 10^{-7}$ Ω·m. It is obvious that values ρ and α dependent on each other. If the ρ is lower, the sample has also better value of α and on the contrary. We can define that the average value of ρ is ≈2× higher than the bulk material value, which is excellent for ≈ 80 nm thick layer. On the other side, the α was in the range from ≈ $2.3 \cdot 10^{-3}$ K^{-1} to ≈ $3.0 \cdot 10^{-3}$ K^{-1} which is reaching ≈ 71 % of bulk material value. This result is also good for such a thin film.

3. CONCLUSION

We presented a method to prepare the stress-free, pure [001] preferentially oriented Ti thin films with low ρ and good value of α deposited using the Kaufman ion-beam source. The experiments showed that BV and *T* have essential influence on crystallography, lattice parameters and residual stress of prepared Ti thin films.

The BV has significant influence on crystallography. All the samples have [001] orientation. We found that with increasing BV in the range from 200 V to 1200 V increases the presence of [100] towards to BV = 1200 V, where small contribution [101] plane is also present. The sample deposited at BV = 200 V shows only small presence of [100] plane along the [001]. We set constant ion-beam source settings for the next part of experiments where we changed the *T*.

We found that the *T* has essential influence on residual stress and obvious impact on crystallography. The compressive residual stress was reduced with increasing *T* from ≈ 150 °C towards the value of ≈ 295 °C where the tensile stress was reached. Samples deposited in the range of *T* from ≈ 155 °C to ≈ 273 °C show pure [001] orientation, while the sample deposited at ≈ 293 °C showed small contribution of [101] plane along the significant [001] plane. The stress-free sample was deposited at *T* ≈ 273 °C and had also the lowest FWHM of ≈ 0.27° and the highest diffraction peak. We determined the corresponding lattice parameters of this stress-free sample as $a_0 = (2.954 \pm 0.003)$ Å and $c_0 = (4.695 \pm 0.001)$ Å.

We measured the ρ and α electrical properties of all samples from second series. We obtained excellent results of electrical properties for ≈80 nm thick layer. The value of the ρ was in the range from ≈ $8.0 \cdot 10^{-7}$ Ω·m to ≈ $10.2 \cdot 10^{-7}$ Ω·m which is ≈ 2× higher than the bulk material value. The value of α was in the range from ≈ $2.3 \cdot 10^{-3}$ K^{-1} to ≈ $3.0 \cdot 10^{-3}$ K^{-1} reaching ≈ 71 % of bulk material value. These electrical parameters for stress-free sample with pure [001] orientation were $\rho = (9.2 \pm 0.1) \cdot 10^{-7}$ Ω·m and $\alpha = (2.6 \pm 0.2)$ K^{-1}.

The presented behavior and properties of Ti thin films especially the parameters of stress-free sample are attributed to deposition by the Kaufman ion-beam source at specific deposition conditions. These thin films are well suitable for MEMS applications. Furthermore, such a high quality properties are not achievable by the conventional magnetron sputtering technique.

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