

## Texture change of TiN films due to anisotropic incorporation of oxygen

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### ABSTRACT

Results of comprehensive structural and microchemical analyses revealed the mechanisms responsible for changing the  $\langle 111 \rangle$  to  $\langle 001 \rangle$  competitive growth texture of TiN films when the level of oxygen doping was 20 at.%. It has been shown that the growth competition is related to the different way of segregation-incorporation of the oxygen species on the  $\{001\}$  and  $\{111\}$  crystal faces. Oxygen is preferentially segregated on the  $\{111\}$  crystal face and is growing in the form of a 2D TiO<sub>2</sub> surface layer on the growth surface, limiting the growth of  $\langle 111 \rangle$  oriented crystals. On the  $\{001\}$  faces, however, the major part of condensing oxygen species is dissolved into the crystal lattice and only a part forms TiO<sub>2</sub> aggregates. These aggregates have a 3D morphology which do not hinder the growth of  $\langle 001 \rangle$  oriented crystals. Consequently, the  $\langle 001 \rangle$  oriented crystals win the growth competition leading to a film structure constituted of V-shaped columns.

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### 1. Introduction

The effects of in-situ oxygen doping on the morphology and texture of TiN thin films and the binding state of incorporated oxygen have been investigated by numerous authors [1–10]. It is generally experienced that the structure is modified: the texture changed from  $\langle 111 \rangle$  to  $\langle 001 \rangle$  with increase of oxygen. It has been found that the change of the  $\langle 111 \rangle$  texture to  $\langle 001 \rangle$  occurs if the oxygen concentration is higher than 15 at.% [3,11,12]. A new sub-structure has been discovered in the single crystalline columns of the TiN film doped with 20 at.% oxygen grown with  $\langle 001 \rangle$  texture [13].

Ehiasarian et al. reported on the development of  $\langle 001 \rangle$  texture in TiN film deposited by high power impulse magnetron sputtering (HIPIMS) [14]. In these experiments the deposition started at high oxygen partial pressure (as contamination related to the degassing of the system) incorporating ~18 at.% oxygen and after the degassing, as the oxygen pressure decreased, the concentration of incorporated oxygen is decreased to 2 at.%. The volume fractions of crystals at the surface of the film with random,  $\langle 001 \rangle$  and  $\langle 111 \rangle$  orientations were 10%, 64% and 26% respectively. These indicated

that the development of the  $\langle 001 \rangle$  texture started but had not completed at this film thickness. Considering the V-shaped morphology of the  $\langle 001 \rangle$  oriented single crystal columns Ehiasarian et al. suggested that the  $\langle 001 \rangle$  texture could be developed by competitive growth [14]. However, the mechanisms which could control the competitive growth at oxygen doping beyond a critical level has not been clarified yet.

The aim of the present work was to collect structural information on oxygen doped  $\langle 111 \rangle$  and  $\langle 001 \rangle$  oriented TiN films which could validate the competitive nature of the growth of crystals responsible for the texture development. These results could lend support to reconstruct the atomic processes and growth phenomena for understanding why the  $\langle 001 \rangle$  oriented crystals dominate the competitive growth beyond 15 at.% oxygen doping. A series of samples with increasing oxygen concentration was prepared at the same deposition parameters and investigated. Authors considered that the quantity of oxygen incorporating during the film growth controls the structure evolution directly and not the oxygen partial pressure (more precisely the relative impinging rate of oxygen species), which would be very difficult to determine quantitatively. That is why the results were analyzed in dependence of the incorporated oxygen concentration and not as a function of the oxygen partial pressure during the deposition. Only films with homogenous oxygen concentration distribution along the thickness have been considered. In the present paper results on three

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samples are reported. The first (TNO-4) is a sample containing 4 at.% oxygen as environmental contamination with well developed  $\langle 111 \rangle$  texture. The second (TNO-11) was deposited at increased oxygen pressure and incorporated 11 at.% oxygen grown also with  $\langle 111 \rangle$  texture. The third sample (TNO-20) contained 20 at.% oxygen and grown with well developed  $\langle 001 \rangle$  texture. By this way we intended also to prove that the variation of the texture is indeed related to the oxygen doping.

## 2. Experimental details

Titanium nitride thin films with thicknesses around 1.3  $\mu\text{m}$  were deposited in a home made laboratory scale magnetron sputter unit (Fig. 1A). The octagonal all-metal high vacuum chamber of 75 l volume was evacuated by a 540 l/s turbo-molecular pump producing  $2 \times 10^{-4}$  Pa background pressure. Three independent unbalanced magnetron sputter sources were closely arranged side by side on the neighboring vertical walls. The magnetic fields of closely disposed magnetron sources arranged on an arc segment were highly interacting, leading to a far extended active plasma volume. In the present deposition experiments only the centrally positioned magnetron source was applied. A planar rectangular metallic Ti target ( $165 \times 85 \times 12 \text{ mm}^3$  in size) of 99.95% purity (PLANSEE GmbH) was used. The discharge plasma was excited reactively in a mixture of Ar,  $\text{N}_2$  and  $\text{O}_2$  by a close-loop controlled dc power supply. The discharge power for each deposition run was 500 W [15]. The Ar gas flow rate was stabilized by a solenoid valve actuated mass flow controller (MFC-Granville Phillips S 216), and measured by a GFM 17 Aalborg mass flow meter. The nitrogen flow rate was controlled by Aalborg DFC 26 digital mass flow controller. Introduction of oxygen gas was manually controlled by using a high precision needle valve (Granville Phillips type). In the deposition process the total pressure of mixed gases was maintained at constant value by changing the conductance in down stream of the gases via adjusting a throttle valve in the pumping system. The throttling was 30% and the background pressure was  $3.4 \times 10^{-4}$  Pa at this throttling. The non-doped sample (TNO-4) discussed in the present work was deposited in a mixture of Ar +  $\text{N}_2$  atmosphere with a total pressure  $P_{\text{N}_2} + P_{\text{Ar}} = 0.5$  Pa. The flow rate of  $\text{N}_2$  was 3 sccm establishing  $P_{\text{N}_2} = 0.1$  Pa partial pressure. Titanium-oxynitride thin films have been prepared at the same nitrogen and Ar flow rates while the oxygen flow rate was varied. The partial pressure of oxygen before starting the deposition was  $4 \times 10^{-2}$  Pa in case of sample TNO-20 while in case of sample TNO-11 it was  $3.3 \times 10^{-3}$  Pa.

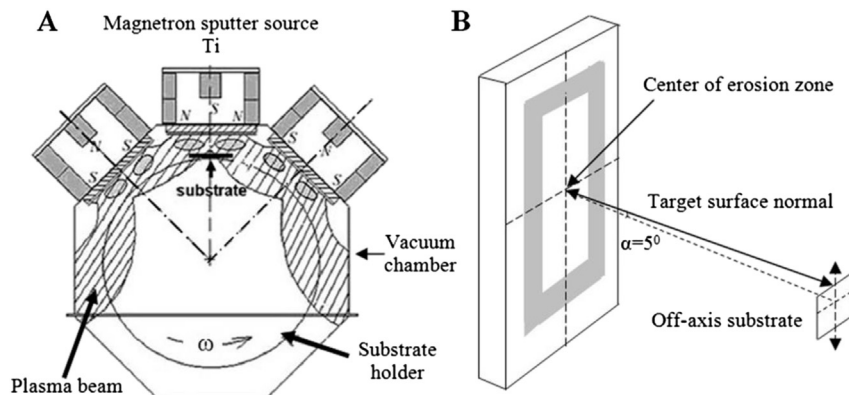
The films were deposited at 400 °C substrate temperature at 0.2  $\text{nm s}^{-1}$  on  $20 \times 20 \text{ mm}^2$   $\langle 001 \rangle$  oriented Si single crystal

substrates covered by a native oxide. The substrates were positioned in front of the sputter source at a distance of  $d_{\text{T-S}} = 110 \text{ mm}$  slightly off the normal of the geometric center of the cathode according to the arrangement shown in Fig. 1B. This resulted in small angle oblique incidence of the species emitted by the cathode. The thickness and growth rate of the deposited thin films were measured by an oscillating quartz crystal monitor. Prior to deposition the target surface was plasma-etched for 10 min at 0.8 Pa by dc glow discharge in argon atmosphere. During the sputter cleaning of the target surface the substrate was shielded.

The microstructure of the films was investigated by X-ray diffraction (XRD) and by transmission electron microscopy techniques. For XRD analysis a Bruker AXS D8 Discover diffractometer equipped with Göbel-mirror and a 2D position sensitive (GADDS) detector system with Cu  $K\alpha$  radiation were used [16]. The intensity was acquired at four detector positions at nominal  $2\theta$  angles of 20°, 40°, 60° and 80°, covering the range of about 7°–93°, while the samples were positioned at  $\theta = 10^\circ, 20^\circ, 30^\circ$  and  $40^\circ$ , respectively. In the present diffraction patterns the Si 400 reflection is not shown because the measurements have been carried out at sample position  $\theta = 30^\circ$  and not at  $\theta = 34.56^\circ$ .

Electron-microscopic investigations were carried out both on cross-sectional (X-TEM) and plan-view specimens prepared by mechanical cutting, grinding and ion beam thinning techniques [17,18]. With the target–substrate arrangement used in our facility (see Fig. 1B) a fraction of the vapor species was impinging at oblique incidence. Therefore tilted growth of columns towards the normal of the cathode may be expected. The mechanical cutting of X-TEM specimens was taken along the direction as shown in Fig. 1B to show the columns in their full length. A Philips CM20 transmission electron microscope working at 200 kV and equipped with a Ge-detector NORAN EDX analyzer was applied for the conventional TEM investigation and chemical analysis. The high-resolution TEM investigation was carried out in a 300 kV JEOL 3010 TEM. Selected area electron diffraction (SAED) was applied to analyze the variation of the texture along the thickness of the film. The “ProcessDiffraction” software [19–21] made possible both the qualitative and quantitative evaluation of the selected area electron diffraction patterns. Reflection high energy electron diffraction (RHEED) made it possible to determine the orientation of crystals penetrating to the surface of the film.

Precession electron diffraction (PED) data sets were recorded using a TECNAI G2X transmission electron microscope (TEM, LaB6 cathode, 200 kV, 1° precession angle) to acquire orientation information on crystallites [22,23]. For data acquisitions a  $2.5 \times 2.0 \mu\text{m}^2$  area scanned with step size of  $10 \times 10 \text{ nm}$  and the diameter of the beam was kept below 5 nm. The orientation mapping (ASTAR



**Fig. 1.** Scheme of the octagonal all-metal sputter system evacuated by a turbo molecular pump (A) and the substrate – target arrangement (B). The off-axis position of the substrate is shown. The direction of the mechanical cutting of the X-TEM specimens is marked by an arrow.

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