Effect of Oxygen doping on Titanium Nitride thin films prepared by reactive unbalanced magnetron sputtering

Ph.D. Thesis

Mohamed Fathy Hasaneen

Doctoral School of Physics
Head: Prof. László Palla

Doctoral Program of Material Science and Solid State Physics
Head: Prof. János Lendvai

Doctoral Program of Material Science and Solid State Physics

Head: Prof. János Lendvai

Supervisor Prof. Péter B. Barna

Hungarian Academy of Sciences
Research Centre for Natural Sciences
Institute for Technical Physics and Materials Science

Eötvös Loránd Tudományegyetem

BUDAPEST

2013

1. Motivation

Titanium Nitride (TiN) is one of the most widely applied surface coating. TiN coatings are generally prepared by PVD (Physical Vapor Deposition) techniques. The structural and morphological properties of TiN films depend mainly on the preparation parameters and type of dopant (including contamination) which are incorporated during the film growth. One of the most important dopant is the Oxygen. It is also because Oxygen is the most general contamination in case of PVD deposition techniques and can be present at unexpected high level (up to 20 at.%) in the first stage of deposition if the degassing of the deposition system is not carefully done. On the other hand is has been also shown that a minute amount of Oxygen contamination hinders the formation of stable nanostructure in TiN/Si_3N_4 nanostructures. In TiN films prepared at substrate temperatures $0.2 < T_s/T_m < 0.3$ (Zone T) the <111> preferred orientation (PO) is the most commonly observed orientation of growth, however <001> and <220> PO have also been reported by changing the deposition parameters such as bias voltage N/Ti ion ratio, the ratio of N^+/N_2^+ and the oxygen doping. It has been pointed out that at oxygen contamination beyond 15at.% the 111 texture is changing to 001. On the other hand, Oxygen is used as additive to prepare oxynitride thin films. Therefore, it is important to understand the detrimental role of oxygen contamination in the structure evolution. Though there are case studies presenting information on the effect of oxygen additive on the structure and properties of TiN films the comprehensive structure characterization of the oxygen doped TiN films and the analysis by which mechanisms the oxygen can influence the structure evolution are practically missing.

2. Aim of this work

The aim of this work is to follow the effect of oxygen additive on the structure and the texture evolution in TiN films deposited by reactive unbalanced magnetron sputtering. Experiments were carried out in the 0 < 20 at.% Oxygen concentration range. The structure and structure evolution were investigated in details both in undoped films and in films with 20 at.% oxygen content to be able to understand the influence of oxygen on the structure and on the fundemental phenomena of film growth. As an application of these results it has been shown that crossover can develop between the 001 and 111 textures when changing the oxygen concentration during the film deposition.

For realizing a more comprehensive characterization of the film structure various methods were applied:

1. Cross-section(X-TEM), plane view transmission electron microscopy and selected area diffraction (SAED),
2. PED-ASTAR techinque adapted to the TEM for visuailizing the local orientation of crytals,
3. Energy dispersive X-ray microanalysis (EDX),
4. X-ray diffraction (XRD),
5. Auger (AES) and X-ray photoemission spectroscopy (XPS),
6. Atomic force microscopy (AFM),
7. Ultra-Micro-Indentation system (UMIS),
8. ProcessDiffraction computer program for quantitive determination of the phases and the degree of texture.

3. New scientific results

1. By dedicated experiments and comprehensive structure analysis of $Ti_{0.45}O_{0.20}N_{0.35}$ film I have confirmed and demonstrated the competitive growth mechanism of the

001 texture evolution proposed in the literature. [P1, P3, L1 – L6]

1.1 I confirmed that in the applied deposition system and deposition parameters (substrate temperature, deposition rate, N and Ar pressure) the undoped TiN films are growing with 111 fiber texture perpendicular to the substrate.

1.2 By this way I demonstrated unambiguously that the change of the 111 texture to 001 is directly related to the oxygen doping.

2. I have shown at first that one part of incorporated oxygen is present in segregated TiO_2 phase and determined its distribution. [P2, L5, L7].

   2.1 The TiO_2 phase is situated both at the boundaries of the V-shaped TiN single crystal columns and within their bulk.

   2.2 The TiO_2 phase incorporated into the bulk of single crystal columns segregated in discrete fibers parallel to the axes of columns; the fibers are distributed in a honey comb-like network in the cross section of the columns.

3. I concluded that the variation of the 111 texture to 001 at increased oxygen concentration could be related to the different surface chemical interaction of oxygen on the {111} and {001} TiN crystal faces resulting in the faster growth rate of the <001> oriented crystals. The most probable difference could be that on the {001} crystal faces the oxygen is incorporated into the growing crystal lattice by subsurface adsorption while on the {111} faces it is segregated and forms a surface oxide phase limiting the growth of the <111> oriented crystals [P3, L5].

4. By detailed structure analysis of TiN thin films prepared at varied oxygen concentration I could demonstrate at first

the crossover between the 001 and 111 textures. [P4, L4, L5,L8]

   4.1 The thickness domain developed on the substrate at 20at.% oxygen is with 001 texture, while the second thickness domain with 11at.% oxygen beyond of that is with 111 texture.
   4.2 Both domains are composed of crystals with V-shape upwards indicating their competitive growth.
   4.3 Between the two domains with textures there is a thickness domains in which both textures coexist but the 001 oriented crystals are with V-shape morphology down while the 111 oriented crystals are V-shaped upwards. These shape morphologies clearly demonstrate that the <001> oriented crystals are deceased and overgrown by the <111> oriented ones. That thickness domain is the crossover between the two textures.

5. I have shown by dark field X-TEM imaging that the <111> oriented crystals present in the upper thickness domain are nucleated on the substrate. I concluded that a crossover between the 001 and 111 textures can develop when the oxygen concentration is decreased at the growth stage at which <111> oriented crystals are still present surviving the first competitive growth regime dominated by faster growing <001> oriented crystals. [P4, L4, L5, L8].

4. Publications of our results

4.1. Scientific papers

P1. Effect of oxygen doping on the evolution of 001 texture and the crossover between 001 and 111 textures in TiN films,

D. Biró, **M. F. Hasaneen**, L. Székely, M. Menyhárd, S. Gurbán, P. Pekker, Dódony, and P. B. Barna,
Yearbook 2011 for Research Institute for Technical Physics and Materials Science-Hungarian Academy of Sciences.

P2. Substructure in the columnar crystals of the $Ti_{0.45}O_{0.2}0N_{0.35}$ Oxynitride thin film
M.F. Hasaneen, D. Biro, L. Székely, P. Nemes-Incze1and P.B. Barna,
Vacuum, 86 (2012)2105-2108.

P3. Evolution of the 001 texture in $Ti_{0.45}O_{0.2}0N_{0.35}$ oxynitride thin film
D. Biro, **M.F Hasaneen**, L. Székely, M. Menyhárd, S. Gurbán, P. Pekker, I. Dódony, P.B. Barna,
in preparation.

P4. Development of the crossover between 001 and 111 textures in TiN films due to the variation of oxygen concentration
D. Biro, **M.F Hasaneen**, L. Székely, M. Menyhárd, S. Gurbán, P. Pekker, I. Dódony, P.B. Barna,
in preparation.

4.2 Lectures presented at conferences

L1. Influence of Oxygen doping on titanium nitride thin films prepared by DC magnetron sputtering,
M. F. Hasaneen,
International workshop for PhD student, Austria, Vienna, 2 May 2011.

L2. Effect of oxygen doping on the structure evolution of TiN thin film,
M.F. Hasaneen, D. Biro, L. Székely, M. Menyhárd, S. Gurbán, P. Pekker, I. Dódony, P.B. Barna,

International workshop for PhD student, Prague, Czech Republic, 2 May 2012.

L3. Effect of oxygen on the structure evolution of TiN thin films deposition by unbalanced magnetron sputtering,
M.F. Hasaneen, D. Biro, L. Székely, M. Menyhárd1, S. Gurbán, P. Pekker, I. Dódony, P.B. Barna,
Hungarian National Conference on Microscopy, SIÓFOK, LAKE BALATON, 10-12 May 2012.

L4. Effect of oxygen doping on the evolution of 001 texture and the crossover between 001 and 111 textures in TiN films,
D. Biro, **M.F. Hasaneen**, L. Székely, M. Menyhárd, S. Gurbán, P. Pekker, I. Dódony, P.B. Barna,
International conference on thin film physics, JVC-14/ EVC-12/AMDVG-11/CroSloVM-19 Conference, Dubrovnik, Croatia, 04-08 June 2012.

L5. The role of dopants in the formation of nanograin Thin Film Materials**,**
P.B. Barna, D. Biro, F. Misják, **F.M. Hasaneen,** L. Székely, G. Radnóczi,
The 67^{th} IUVSTA Workshop "High temperature amorphous and nanostructure ceramic coating: challenges and opportunities" CERAMAX) in Manchester, 23-27 September, 2012.

L6. Evolution of 001 texture under effect of oxygen concentration,
D. Biro, **M.F Hasaneen**, L. Székely, M. Menyhárd, S. Gurbán, P. Pekker, I. Dódony, P.B. Barna,
International workshop for PhD student, Austria, Vienna, May 2013.

L7. Substructure in the columnar crystals of the $Ti_{0.45}O_{0.20}N_{0.35}$ oxynitride thin film,

M.F. Hasaneen, D. Biro, L. Székely, P. Nemes-Inczeand P.B. Barna,
Hungarian National Conference on Microscopy, SIÓFOK, LAKE BALATON, 23-26 May 2013.

L8. Crossover between the 001 and 111 textures in TiN hard coatings related to the variation of the oxygen concentration,
D. Biro, **M.F. Hasaneen**, L. Székely, M. Menyhárd, S. Gurbán P. Pekker, I. Dódony, P.B. Barna,
Hungarian National Conference on Microscopy, SIÓFOK, LAKE BALATON, 23-26 May 2013.