Coating The Inner Walls Of Tubes With TiN Films By Reactive Sputtering

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Abstract. It is possible to achieve a homogenous coating of the inner walls of tubes by sputter deposition. For this purpose a conical sputter target is moved through the tube parallel to its axis while an ion beam enters the tube along its axis, impinges onto the target and sputters material onto the tube inner wall. But so far only monatomic coatings were performed with this technique.

To improve the mechanical properties of tubes TiN films were deposited by reactive sputtering. Therefore a Ti sputter target is used, the N₂ reactive gas is delivered into the tube by a nozzle.

The topography of the films is dominated by a ripple structure with the wave vector perpendicular to the tubes length axis. The development of the ripples is discussed in terms of scattered Ar projectiles which impinge onto the substrate as well as the deposited film under grazing incidence angles. Results of RBS, ERD, AFM, and hardness measurements are shown.

INTRODUCTION

In industries tubes are widely used and often required to exhibit better performance in wear and corrosion behaviour than the base material of which the tube is made. This can be achieved by coating the inner walls with a protective film. Several investigations on coating the inner walls of tubes have been reported [1-6].

In the present paper a reactive sputtering process is used to deposit TiN thin films on the inner walls of tubes. This technique enables the coating of the tubes with a large variety of materials and compounds at low substrate temperatures combined with the advantages of the sputtering process such as low porosity and enhanced adhesion of the films.

In the following, an overview of the properties of TiN thin films deposited by reactive sputtering onto the inner walls of silicon and stainless steel tubes is given.

EXPERIMENTAL

The homogenous coating of the inner walls of tubes with a high ratio of length/diameter with common facilities is rather difficult. The atoms to be deposited have to enter the tube under very flat angles. In this case screening effects lead to inhomogeneities of the film thickness. To overcome this drawback, the source of the deposited material, shaped as a conical sputter target (outer diameter 15 mm, cone angle 60°), is placed into the tube. For a homogenous coating of the whole tube (inner diameter 16 mm, length 140 mm) the target is rotated while the target is hit by an ion beam incident parallel to the tubes longitudinal axis (details in Ref. [8]). The sputtered target atoms are re-deposited onto the inner tube walls. A portion of the ions is backscattered from the target and impinges the growing film where typical ion beam effects such as structural and compositional changes are initiated. Due
to the gas inlet for reactive sputtering scattering processes between the projectiles and the gas molecules take place and lead to an additional bombardment of the growing film with energetic projectiles. The processes taking place during film deposition are shown schematically in Fig. 1.

FIGURE 1. Schematic presentation of the processes which take place during the reactive ion beam sputter coating of the inner walls of tubes: (1) Tube to be coated, (2) Ti-sputter target (3) Nozzle for N₂ gas inlet (4) Deposited TiN (5) Sputtering of Ti-particles (6) Scattering of Ar⁺ projectiles by N₂ molecules (7) Backscattering of projectiles from the target surface, which can impinge on the substrate surface at a maximum distance x=0.9 mm measured from the outer diameter of the target cone.

The deposition of 200 nm thick TiN coatings onto the inner walls of tubes is realized by moving a conical Ti sputter target (99.99% purity) through the tube. The N₂ reactive gas with a flow rate of 10 sccm is delivered into the tube by a nozzle with leads to a gas pressure of 8x10⁻³ Pa in the preparation chamber. The residual pressure in the preparation chamber was 1x10⁻⁵ Pa. Seven substrates of size 10x20 mm were set in a metal tube along the length axis of the tube. Due to the tube rotation the deposited films show a good homogeneity along the circumference as shown for copper thin films in [8]. The properties of the TiN films are reported not to be closely related to the substrate materials [7]. Thus silicon (100) and glass was chosen as a substrate for Rutherford backscattering spectrometry (RBS), elastic recoil detection (ERD) and atomic force microscopy (AFM) measurements and stainless steel for the investigation of the film hardness. In all cases Ar⁺ ions were used as sputtering species, the rotation speed was 100 min⁻¹. While the beam current into the tube was held constant at 50 µA for all deposition processes, the ion energy was varied from 40 keV to 180 keV which leads to an increase of substrate temperature from ~80°C to ~180°C, respectively.

Results and discussion

Homogeneity of film thickness

As published earlier the set-up used makes possible to achieve film thickness homogeneities along the circumference and along the longitudinal axis of the tube better than 5% [8]. The additional gas inlet during TiN reactive sputter deposition results in higher nitrogen gas pressures inside the tube than measured in the preparation chamber. This leads to scattering processes of projectile ions with nitrogen molecules which are characterised by small scattering angles (No. 6 in Fig. 1). Scattered projectiles do no longer impinge at the target surface but at the tube. Because of the electric shortening of the tube and the target which is necessary for beam current measurement, those scattered ions can’t be distinguished from ions hitting the target. With increasing length of flight into the tube more projectiles are scattered onto the tube inner wall and do not contribute to film deposition, but influence the film topography (see below). This leads to a decrease in film thickness with increasing position in the tube (measured from the entrance hole of the ion beam) which can be compensated by a position dependent feed rate, as shown in Fig. 2. With an increase of ion energy this effect decreases because of the decrease of scattering cross section and has no measurable influence for ion energy 180 keV. The homogeneity along the circumference is not influenced by ion scattering processes.

FIGURE 2. Amount of deposited Ti along the longitudinal axis of the tube at 40 keV ion energy(open circles) and constant feed rate, 40 keV and position dependent feed rate (full circles) and 180 keV and constant feed rate (open triangle), measured by RBS.
Composition

The influence of ion energy on the chemical composition of thin TiN films was analyzed by ERD.

![Graph showing element concentration vs. ion energy](image)

**FIGURE 3.** Variation of the chemical composition of TiN films with increasing ion energy, measured with elastic recoil detection (ERD).

Fig. 3 shows that the nitrogen content decreases with increasing ion energy. Simultaneously the oxygen content increases, so that the stoichiometric composition for Ti and N of 1:1 is reached only for an ion energy of 40 keV. The carbon content varies between 0.5 at.% and 2 at.% and the argon content between 0.5 at.% and 1 at.%.

The decrease of nitrogen content with ion energy can be explained by means of decreasing collisional energy deposition at the growth surface with increasing ion energy. Energy deposition at the growth surface is necessary to overcome the activation barrier of physisorbed nitrogen for the TiN compound formation [9-11]. By increasing the ion energy the energy delivered to the substrate by ions reflected at the target surface (No. 7 in Fig. 1) or scattered at N$_2$ molecules (No. 6 in Fig. 1) increases. Nevertheless the nitrogen content decreases. There are two possible reasons. 1) As TRIM [12] calculations show, the increase of ion energy leads to an increase of the energy of projectiles backscattered from the target. Thus their energy is deposited at increasing depth and therefore does contribute less to the activation of adsorbed nitrogen. 2) From the measurements of film homogeneity one can conclude that with an increase of the ion energy the amount of projectiles scattered from the N$_2$ molecules decreases and the amount of ions bombarding the growing TiN film decreases.

Hardness

With increasing ion energy from 40 keV to 180 keV the TiN film hardness decreases from 20.5 GPa to 15.3 GPa. This is an improvement by a factor of 2.3 to 3 compared with the uncoated stainless steel substrate. The values are close to the hardness of a TiN(111) single crystal of approximately 21 GPa [13]. With increasing ion energy an increase of oxygen content of the films is also observed (Fig. 3). To test the influence of oxygen, a TiO$_x$N$_y$ film with an oxygen and nitrogen content of 54 at.% and 6 at.% respectively was deposited at 180 keV. This film shows a hardness of only 11 GPa. Thus the increasing oxygen content is supposed to be a reason for the decrease of film hardness with increasing ion energy. The surface roughness may influence the hardness measurement, too, since the indentation depth was only 20 nm.

![Graph showing hardness vs. ion energy](image)

**FIGURE 4.** Variation of the hardness of TiN films with increasing ion energy (full circles), substrate hardness (solid line) and hardness of a TiO$_x$N$_y$ film (open circle).

Topography

The topography of TiN films was determined by AFM measurements (Fig. 5). Films deposited with ion energy of 40 keV show stripe structure which degrades with increasing ion energies. This structure develops due to an ion bombardment of the substrate with ions scattered at the N$_2$ molecules (No. 6 in Fig. 1). These scattered projectiles incident at the tube wall at grazing incident angles. Due to a surface curvature dependent sputtering yield and screening effects a ripple structure with a wave vector perpendicular to the surface projection of the incident ions develops [14].
The development of the observed topography can be explained in two steps.
1) The ripple structure initiates at the uncoated substrate behind the maximum range $x$ which can not be reached by ions backscattered from the target surface (see Fig. 1). This is demonstrated in Fig 6a showing an atomic force micrograph of an uncoated Si(100) substrate taken at the position $x+2$ mm of a tube which was not coated at full length.
2) With ongoing target movement the deposition process starts at prestructured substrate areas and the surface topography is transferred to the film. The wavelength of the structure of the TiN film is determined by the wavelength of the ripples at the substrate surface. This can be seen in Fig. 6 a-d showing AFM images of TiN films prepared at equal deposition parameters on Si(100) (Fig. 6a, b) and glass (Fig. 6c, d). For different substrates Bradley et al. predict a different wavelength at identical ion bombardment parameters [14] because of differences in the material dependent energy deposition profiles. For one single substrate material the wavelength on substrate and the TiN film are identical. When changing the substrate material, the wavelength of both, the substrate topography and the film topography change in the same manner.

CONCLUSION

Inner tube walls were homogenous coated with TiN films by reactive ion beam sputtering. The deposited TiN films show a nearly stoichiometric N/Ti ratio, hardness close to the value of a TiN (111) single crystal and a ripple structure at the film surface. These properties decrease with an increasing energy of the sputtering ions. This is discussed in terms of a decreasing scattering cross-section of Ar ions with gas molecules, resulting in reduced ion bombardment of the growing film at higher energies.
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REFERENCES