Electrical properties of titanium nitride films synthesized by reactive magnetron sputtering

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Abstract. Reactive dc magnetron sputtering was employed to produce thin films of titanium nitride using titanium metallic target, argon as the plasma gas and nitrogen as the reactive gas. A set of the films was studied deposited on the Si, fused silica and crystalline (001) MgO substrates with various deposition conditions. The films deposited on the Si and SiO₂ substrates are polycrystalline while deposited at slow rate to the heated to 600°C MgO substrate are highly epitaxial according both to XRD and LEED data. Electrical resistivity of the films was measured by means of the four-probe van der Pauw method.

1. Introduction
Titanium nitride (TiN) is a material that for a long time is used in many technological, medical and scientific fields due to its outstanding properties. Recently, it has been found that TiN thin films may serve also as the plasmonic materials that can hold the temperatures much higher than the classic plasmonic elementary compounds like gold, silver or copper [1]. Owing to its outstanding physical properties such as high hardness, modulus of elasticity, thermal expansion coefficient and a transition to superconducting state [2, 3], TiN is an attractive material for application in various photoelectric devices [4, 5]. Also, some important features of titanium nitride such as good wear resistance, high corrosion resistance, low friction coefficient, high conductivity and a bright, golden color enabled it to be used in protective and functional coatings on cutting tools, bearings, etc [6]. Due to high electrical conductivity and thermal stability of TiN film, TiN coating has recently been led to electrodes in microelectronic devices [7]. Titanium nitride is well known for lustrous golden color [8] which is useful for decorative applications. Golden color is a result of the high reflectance of TiN at the red end of the visible part of spectrum with low reflectance near the ultraviolet region. This makes it a potential coating for IR-reflective back contacts material and a solar energy absorber suitable for solar cells [9]. In addition, titanium nitride could replace the polycrystalline silicon and be used as a gate electrode in MOS devices [10]. It may be also used in biomedical materials because of its noncytotoxic nature [11].

In this paper, the deposition of titanium nitride films on magnesium oxide, silicon and fused silica substrates by reactive dc magnetron sputtering under the different conditions of deposition will be described. Also, we report the electrical properties of TiN thin films produced by reactive magnetron sputtering.
2. Experimental part

2.1. Synthesis
Titanium nitride (TiN) films were deposited by the reactive dc magnetron sputtering with the power of 30-150 W on the cleaned silicon, fused silica and crystalline magnesium oxide substrates. Titanium metal target with a purity of 99.99% was used for deposition. Before the deposition, the pressure was set to $5 \times 10^{-3} \text{ mbar}$ inside the chamber with desired argon and nitrogen gas partial pressures. The deposition conditions are shown in Table 1.

| Parameter       | Value                   |
|-----------------|-------------------------|
| Power           | 30, 50, 100, 150 W      |
| Deposition time | 30, 60, 120, 180 min    |
| N\textsubscript{2} concentration | 20, 10, 5, 1, 0.99 % |
| Sub. temperature | 25, 500, 600 °C        |
| Base pressure   | $5 \times 10^{-3}$ mbar |

2.2. Characterization

*In situ* XPS measurements were performed in the ultrahigh vacuum chamber (base pressure $\sim 3 \times 10^{-10}$ mbar) equipped with the Mg-K\textsubscript{α} X-ray source operated at 12.5 kV and 250 W, and a Phoibos-150 hemispherical energy analyzer (all from SPECS). The crystal structure and orientation were tested with Bruker D8 Advance X-ray diffractometer with the use of Cu-K\textsubscript{α} ($\lambda = 1.5418$ Å) radiation in the Bragg–Brentano geometry with the scanning rate of 0.002 degree per second in the range of 2θ angles from 17° to 82° and a step of 0.0153°. Surface roughness of the deposited films was measured using atomic force microscopy (NTEGRA-Spectra system by NT-MDT). Low energy electron diffraction (LEED) was utilized to determine the near-surface crystalline structure of the films and of the MgO substrate surface. The resistivity measurements were performed using the van der Pauw four-point probe approach.

After deposition of titanium nitride films, they were analysed by LEED in situ and by X-ray diffraction (XRD) ex situ. Figure 1 shows the XRD pattern of the TiN films on MgO (001) substrates. In figure 2 the LEED patterns are presented of the bare MgO (001) substrate and of the deposited onto it TiN film. Both figure 1 and figure 2 indicate a highly textured epitaxial growth of TiN on MgO due to an almost ideal lattice matching and identical crystal structures of MgO and TiN; lattice constants are respectively 4.212 Å and 4.240 Å [12] ($6a/a = 0.66\%$).

**Figure 1.** XRD pattern of the 86 nm thick epitaxial TiN film deposited on (001) MgO.

**Figure 2.** Surface structure of MgO substrate annealed at 800°C before deposition (top) and TiN/MgO after deposition (bottom).
XPS spectra of Ti 2p and N 1s for titanium nitride films are shown in figure 3. No trace of oxygen was found in the in situ collected XPS data of the as deposited films. However, the presence of oxygen is revealed immediately as soon as the films are exposed to the air. From the spectrum of Ti 2p, we can observe the two peaks that reflect the spin degeneracy of the 2p level (2p3/2, 2p1/2) with the binding energy of 455 eV and 460.8 eV, respectively. These values indicate the TiN formation. Similarly, the spectrum of N 1s with the binding energy of 397.2 eV also indicates the TiN formation [13]. Analysis of the AFM topography of the films deposited on the epi-polished MgO gives the mean surface roughness of the in situ annealed MgO substrate of about 0.4 nm, and of the deposited TiN film onto it 0.8 nm; it is known that the substrate annealing is more practical and effective method for rehabilitating the surface of the substrate [14].

Figure 3. XPS spectra of as-deposited TiN film: (a) Ti 2p-lines and (b) N 1s-line.

2.3. Resistivity measurements
The resistivity measurements were performed using the van der Pauw four-point probe system. As shown in figure 4, the shape of the sample is square with ohmic electrodes connected to the four corners according to the van der Pauw method. The resistivity was calculated from the measured $R_A$ and $R_B$ values as follows [15, 16]:

$$e^{-\pi R_A} + e^{-\pi R_B} = 1,$$

where $R_S$ is the sheet resistance; this can be written as follows

$$\rho = \frac{\pi d}{\ln(2)} \frac{R_A + R_B}{2} f.$$  \hspace{1cm} (2)

Here $\rho$ is the resistivity, $d$ is the thickness and $f$ is a factor depending on the values of $R_A$ and $R_B$. The last can be expressed as:

$$f = \left(\frac{R_A - R_B}{R_A + R_B}\right)^{2k_1} - \left(\frac{R_A - R_B}{R_A + R_B}\right)^{4k_2}$$

where $k_1$ and $k_2$ are the constants:

$$k_1 = \frac{\ln(2)}{2}, \quad k_2 = \left(\frac{(\ln(2))^2}{4} - \frac{(\ln(2))^3}{12}\right)$$

One of the problems that had to be solved was a development of the way to create the resistive connection which was not the case for, e.g., aluminum or gold wire ultrasound bonding. We have found that the best choice among the available to us was the indium/gallium alloy which prompts ohmic contact as shown in figure 5. The changes in resistivity as a function of deposition conditions such as nitrogen flow rate, substrate temperature and thickness were studied as it is shown in Table 2.
Figure 4. Two ways of an electrical connection to the films for measurements of the resistivity by van der Pauw technique.

Figure 5. I-V curve of the films with the indium/gallium alloy bonded electric contacts; dashed line is a linear fit to the data.

Table 2. Values of TiN films resistivity for various deposition conditions.

| Films   | TiN/Si | TiN/SiO₂ | TiN/MgO |
|---------|--------|----------|---------|
| N₂ conc. (%)  | 100    | 20       | 10      |
| Substrate temp. (°C) | 25     | 500      | 500     |
| Thickness (nm)   | 110    | 150      | 150     |
| Resistivity (μΩ-cm) | 130    | 26.1     | 15.4    |

Clearly, the resistivity of the deposited films lies in a wide range and may differ by two orders of magnitude. Typical value of the film resistivity lies in the range of 10-15 μΩ-cm, close to the bulk one. The highest value was obtained for the film deposited on the substrate held at room temperature in the pure nitrogen atmosphere. This is most probably due to the formation, at least, partial, of the dielectric Ti₃N₄ film. The lowest resistivity value among the series was observed for the highly epitaxial TiN film on the in situ annealed (001)-MgO substrate. The observed reduction may be related to the vanishing carrier scattering on the crystalline domain walls or inter-grain boundaries.

3. Conclusions

Titanium nitride films have been prepared in different conditions by reactive dc magnetron sputtering. Formation of the stoichiometric oxygen-free TiN phase is shown by XPS. A highly epitaxial growth of TiN film on the MgO (001) substrate is observed due to the perfect matching between TiN and MgO lattices. The resistivity of the films was measured by van der Pauw technique; low values of resistivity were obtained for deposited films on MgO (001) due to the epitaxial growth.

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