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Electrical and mechanical properties of nitrided sol-gel derived TiO_2 and SiO_2–TiO_2 films

BARBARA KOŚCIELSKA*, LEON MURAWSKI, LESZEK WICIKOWSKI

Faculty of Applied Physics and Mathematics, Gdańsk University of Technology,
Narutowicza 11/12, 80-952 Gdańsk, Poland

The results of measurements of electrical conductivity for titanium–nitride films prepared by the ammonolysis of sol-gel derived TiO_2 and SiO_2–TiO_2 coatings are presented. Sol-gel derived films on silicon and quartz substrates were nitrided by ammonia treatment in the temperature range from 500 to 1200 °C. The dc conductivity of nitrided films has been measured from 10 K to 900 K. It was found that conductivity is related to the amount of TiO_2, which is converted to TiN during ammonolysis. In this way it is possible to change the electrical conductivity of samples by many orders of magnitude. The observed activation energy of the samples containing large amounts of TiN is below 0.1 eV. This indicates that the conductivity mechanism may be interpreted as electrons tunnelling between metallic TiN granules. The mechanical properties were evaluated by a nanoidentometric technique. The results of nanoidentometric measurements confirm an increase in microhardness and Young's modulus for nitrided SiO_2–TiO_2 films containing large amounts of TiN.

Key words: *sol-gel; nitridation; electrical conductivity; Young's modulus*

1. Introduction

In recent years, much attention has been paid to nitride and oxynitride thin films. Nitride and oxynitride thin films are interesting because of their electrical, chemical, mechanical, and dielectric properties. In particular, TiN is a hard coating material with many commercial applications related to its high melting point, hardness, and resistance to corrosion. One common method of preparation of oxynitride films is the thermal nitridation of sol-gel derived films with ammonia (ammonolysis). The coatings obtained by sol-gel methods are especially suitable for amonolysis due to their porosity. The microporous structure allows both a significant incorporation of nitrogen and its distribution throughout the film [1, 2]. The incorporation of TiN in the

*Corresponding author, e-mail: basia@mifgate.mif.pg.gda.pl.

layer may be explained by reactions between ammonia and reduced titanium oxide during ammonolysis. Kamiya et al. [3] proposed that nitridation may proceed via the following sequence of reactions:

$$NH_3 \leftrightarrow 1/2N_2 + 3/2H_2$$

$$TiO_2 + (2 - x)H_2 \rightarrow TiO_x + (2 - x)H_2O$$

$$aTiO_x + bNH_3 \rightarrow cTiN + dH_2O$$

where TiO_x may be TiO, Ti_2O_3, or another reduced titanium oxide. On the basis of these reactions, it can be stated that the reduction of TiO_2 to TiO_x facilitates the agglomeration of TiN on the surface.

This paper is devoted to the electrical and mechanical properties of titanium nitride films prepared by the ammonolysis of sol-gel derived TiO_2 and SiO_2–TiO_2 coatings.

2. Experimental

The starting solution for obtaining $x$$SiO_2$–(100 – x)TiO_2 films (x = 20, 40, 50, 60, 80 mol%) was prepared by mixing tetraethylorthoxysilicate (TEOS) and titanium isopropoxide (TPOT) with ethanol (EtOH), water, and hydrochloric acid as a catalyst in the molar ratio TEOS + TPOT:H_2O:EtOH = 1:4:25. The layers were obtained by dropping (using a burette) this solution on a silicon and quartz substrate. A different preparation method was applied to obtain TiO_2 films. The starting solution was prepared by mixing titanium butoxide with ethanol (EtOH) in the molar ratio 1:5 and acetyloacetone (AcAc) as the complexing agent. The films were deposited on a quartz substrate by spin coating. Finally, the resulting $x$$SiO_2$–(100 – x)TiO_2 and TiO_2 gel layers were dried and then heated at 500 °C for 1 hour. The samples were subsequently nitrided by ammonia treatment in the temperature range from 500 to 1200 °C. The measured thickness of the films amounted 450 nm.

The formation of TiN microcrystals was examined by X-ray diffraction (XRD) with a Philips X'Pert diffractometer system. XRD patterns were taken at room temperature using CuK_α radiation.

dc conductivity measurements of samples containing large amounts of TiN metallic granules were carried out using a typical four-terminal configuration of electrodes. For measurements of films exhibiting high resistance, a pair of circular gold electrodes (electrode distance about 0.25 mm) was vacuum deposited. The dc conductivity from room temperature to 900 K was measured in nitrogen atmosphere.

The nanoindenter technique was applied to investige mechanical properties (Nano Instruments Inc., Knoxville, TN, U.S.A.). The details of this technique are described elsewhere [4]. During the experiment, the apparatus continuously records the displacement and applied load in an ultra-low range (< 1 mN). Hardness and Young's modulus at the depth of 30 nm were calculated from the displacement dependence of the indenter load. Typical load and displacement resolutions were 75 nN and 0.04 nm, respectively. More than 10 indents were performed on each film and the average values of microhardness and modulus were calculated.

3. Results and discussion

It is well known that thin films of pure TiO_2 crystallise in the anatase phase at about 350 °C and in the rutile phase at and above 600 °C [5]. The XRD patterns of a TiO_2 film and a nitrided TiO_2 film are presented in Fig. 1. The pure TiO_2 film was annealed under the same thermal conditions as during ammonolysis. The XRD results for the TiO_2 film indicate that only the rutile phase is present (curve a). The XRD peaks of the nitrided TiO_2 film correspond mainly to the TiN phase, but the Ti_2N phase was also observed (curve b).

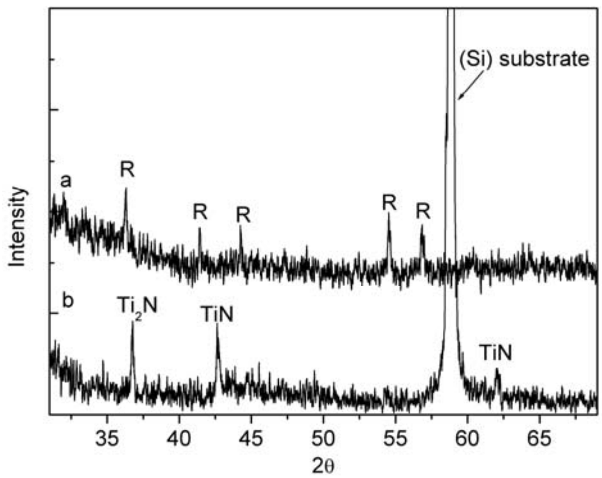

Fig. 1. XRD patterns of a pure TiO_2 film (curve a) and nitrided TiO_2 film (curve b). A pure TiO_2 film was annealed in the same thermal conditions as during ammonolysis

3.1. Electrical properties of poorly nitrided TiO_2 films

In Figure 2, the logarithm of the surface conductivity of the TiO_2 film (annealed under the same thermal conditions as during ammonolysis) and a poorly nitrided TiO_2 film versus the inverse of temperature is presented. Measurements were performed in the temperature range of 450–900 K. The activation energy E_a, calculated from the Arrhenius plot, $\sigma = \sigma_0\exp(-E_a/kT)$, by the least squares method, was about 1.12 eV for the pure TiO_2 sample and 1.14 eV for the nitrided one. The conduction band in crystalline TiO_2 is composed of unoccupied titanium 3d orbitals, while the valence band is formed by filled oxygen 2p orbitals. It is confirmed that oxygen vacancies can be treated as electron donors, which determine n-type conductivity. Measurements

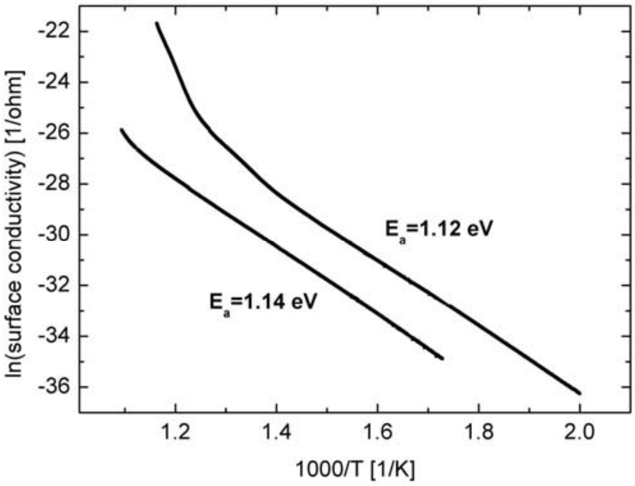

Fig. 2. The logarithm of surface conductivity for a pure TiO_2 film (annealed under the same thermal conditions as during ammonolysis) and a poorly nitrided TiO_2 film versus the inverse of temperature. Measurements were performed in nitrogen atmosphere

were performed in nitrogen atmosphere, and the large value of E_a suggests that bulk oxygen vacancies lying below the conduction band (0.75 eV and 1.18 eV) are responsible for dc transport [6]. A similar conductivity behaviour is observed in poorly nitrided TiO_2 films, for which conductivity is even lower. This may suggest that some oxygen vacancies disappeared during heat treatment in ammonia atmosphere.

3.2. Electrical properties of highly nitrided TiO_2 and SiO_2–TiO_2 films

The results for $x$$SiO_2$–(100 – x)TiO_2 films (x = 20, 40, 50, 60, 80 mol %) and a TiO_2 film containing large amounts of TiN are presented in Fig. 3. The increase in the amount of TiO_2 in the films corresponds to the increased amount of TiN in the nitrided sample. The activation energy of these films decreases from 0.1 eV (for the film containing 20 mol % of TiO_2) to 0.003 eV (for the film containing 80 mol % TiO_2), and the surface conductivity increases by several orders of magnitude. The surface conductivity of these samples varies very little in the entire temperature range. We have previously investigated AFM images of these films, which indicate that the granules of TiN are randomly distributed in the network [7]. This structure is similar to the discontinuous metal structures usually prepared by evaporating or sputtering metal onto a glass surface [8–10]. A commonly accepted theoretical model for electrical conductivity in discontinuous metal structures is based on the tunnelling process of electrons between metal granules [9, 10]. Creation of charge carriers is due to thermal processes leading to the transfer of electrons from one metal granule to neighbouring ones. The energy E_a needed for the creation of two granules, one positively charged and the other negatively charged, is described by the equation

$$E_a = \frac{e^2 F(s,d)}{4\pi\varepsilon\varepsilon_0 d}$$

where d is the diameter of the granules, s is the distance between two granules, ε is the dielectric constant of the matrix, and $F(s,d)$ is a function depending on the distribution of sizes and distances between granules. Calculations of the activation energy for a typical discontinuous metal structure have shown that this value is small, generally below 0.1 eV [9, 10]. This is consistent with the present results of dc conductivity measurements for TiN-containing films with less than 40% TiO_2 (Fig. 3 and Table 1).

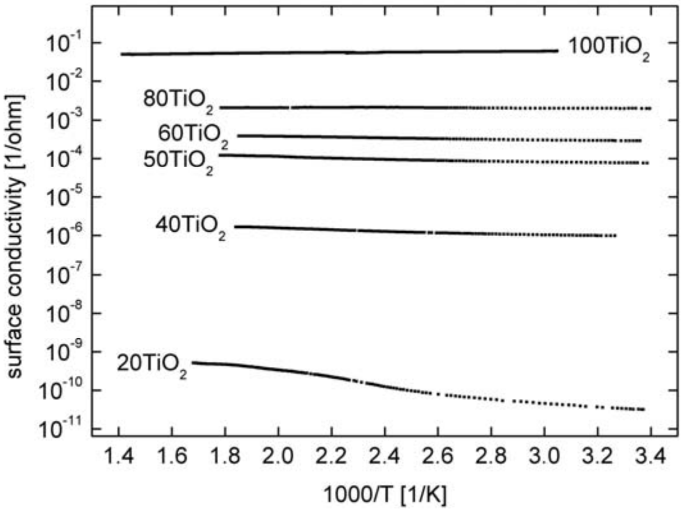

Fig. 3. The surface conductivity of $x SiO_2$–$(100 - x)TiO_2$ nitrided films (x = 20, 40, 50, 60, 80 mol %) and a TiO_2 film containing large amounts of TiN versus the inverse of temperature

Table 1. Conductivity parameters of $(100 - x)SiO_2$–$x TiO_2$ nitrided films (x = 20, 40, 50, 60, 80 mol %). The accuracy of conductivity measurements was about 2%

x [mol %]	Activation energy [eV]	$\sigma_{300\ K}$ [$\Omega^{-1}\cdot cm^{-1}$]	$\sigma_{540\ K}$ [$\Omega^{-1}\cdot cm^{-1}$]
20	0.16±0.002	3.2×10^{-11}	5.0×10^{-10}
40	0.031±0.002	9.9×10^{-7}	1.7×10^{-6}
50	0.026±0.002	7.3×10^{-5}	1.2×10^{-4}
60	0.016±0.002	2.95×10^{-4}	3.9×10^{-4}
80	0.003±0.001	2.05×10^{-3}	2.1×10^{-3}

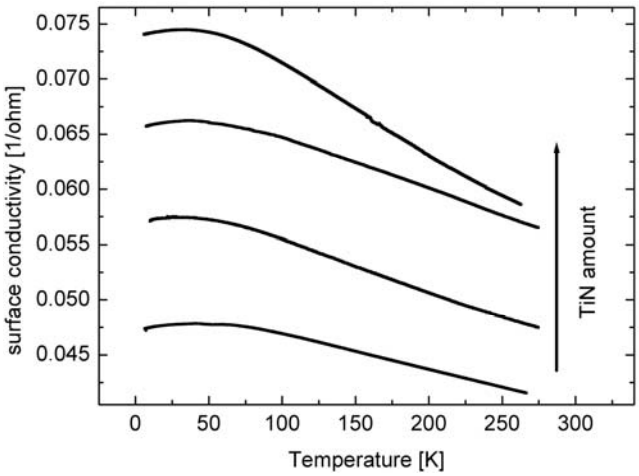

Fig. 4. Surface conductivity versus the inverse of temperature for TiO_2 films with high amounts of TiN metallic granules

TiO_2 films with high amounts of TiN metallic granules exhibit typical metallic behaviour; their conductivity decreases with temperature (Fig. 4).

3.3. Elastic properties of (100 – x)SiO_2–$x$$TiO_2$ nitrided films

The nanoindenter technique was applied to investigate the mechanical properties of films. Figure 5 presents typical load–unload plots for a sample containing 80 mol % of

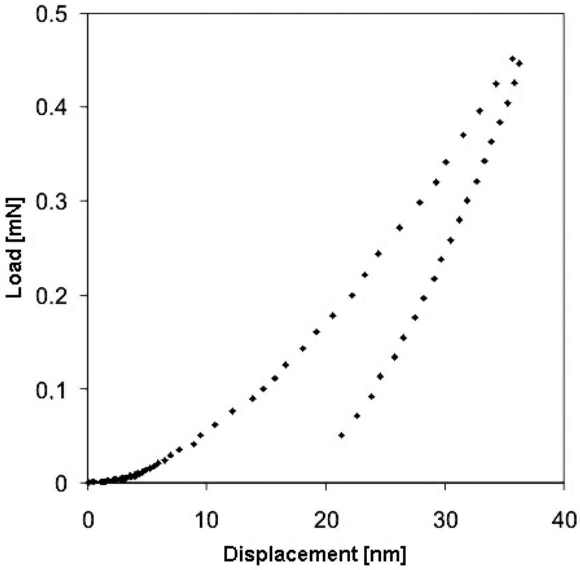

Fig. 5. Indentation load–displacement data for a nitrided TiO_2 (80%)–SiO_2 (20%) film

TiO_2. The elastic modulus *E* of the indented film is calculated from the slope of the unloading curve at the peak load. The hardness *H* is defined by the relationship $H = P/A$, where *P* is the load and *A* is the area of the indent calculated from its plastic depth. The results of calculations for all measured samples are presented in Table 2. The hardness and Young's moduli for these films are similar to those obtained for TiN layers by Oliver et al. [11]. It is found that Young's modulus and hardness increase with titania content and that these values are higher than for silica (E =72 GPa, H = 8 GPa) [4]. This result appears to be consistent with AFM observations [7], which indicate that the surfaces of high-content titania films are almost completely covered by TiN. Therefore, the displacement of the indenter at a depth of 30 nm takes place in TiN and their elastic properties are not very different from pure TiN layers.

Table 2. Young modulus and hardness of the $(100 - x)SiO_2$–$xTiO_2$ nitrided films (x = 20, 40, 50, 60, 80 mol %).

mol% TiO_2	80	60	50	40	20
Hardness [GPa]	18.6±1	14±1	13.7±1	13.8±1	15±1
Modulus [GPa]	240±20	180±20	180±20	180±20	140±20

4. Conclusions

The conductivity of nitrided TiO_2 and SiO_2–TiO_2 films is related to the amount of TiO_2 which is converted to TiN during ammonolysis. In this way, it is possible to change the electrical conductivity of these films by several orders of magnitude. The activation energy of nitrided samples is generally below 0.1 eV. This indicates that the conductivity mechanism may be interpreted as the tunnelling of electrons between metallic TiN granules. TiO_2 films with a high content of TiN metallic granules exhibit decreasing conductivity with temperature, typical of metallic behaviour. The mechanical properties of titania–silica films are improved after nitridation. The films exhibit improved hardness and resistance to scratching. This indicates that TiN nanocrystals are strongly bonded with the matrix.

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