Optical and Electrical Properties of Titanium Oxide Thin Films Deposited by Reactive Magnetron Sputtering Method

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Abstract – Optical and electrical properties of titanium oxide thin films deposited by reactive magnetron sputtering of Ti target in the environment of Ar/O_2 working gas mixture were investigated. The sputtering was carried out at discharge power 1.0 kW in a power stabilization mode. The concentration of O_2 in the working gas mixture varied from 0 up to 50 % at the total pressure of 0.05–0.06 Pa in the chamber. Doped Si (100), optical glasses BK7 were used as substrates. Substrates were located at the distance of 11 cm from the MSS target surface. The films were deposited up to thickness 100–300 nm with the average deposition rate of 0.2–0.3 nm/s.

It was determined, that at high pumping speed the area of magnetron discharge characteristics hysteresis considerably decreased. That allowed stabilizing the reactive magnetron sputtering process without application of special control systems.

The dispersions of refraction index n and extinction coefficient k in the waveband of 245–1650 nm at a different content of O_2 in the mixture of working gases was obtained. The dependences of n and k at the wavelength 0.63 m on content of O_2 in mixture of working gases were estimated.

It was determined, that the reactive magnetron sputtering method makes possible the reproducible deposition of titanium oxide films with refractive index in the range of 2.34–2.38 and the extinction coefficient in the range of 0.006–0.02.

Dielectric characteristics of TiO_2 films were investigated. The dielectric constant and dielectric loss tangent of films were estimated on test structures representing capacitors with the capacitor coating area of 0.64 mm^2. The dependences of dielectric constant and dielectric loss tangent of films on O_2 concentration in the working gas mixture were determined. TiO_2 films were obtained with the value of dielectric constant of 25–38 and loss angle of 0.01–0.02.

It was concluded that these films may be used as optical coatings and dielectrics of capacitor structure for integrated circuits.

1. Introduction

The titanium oxide (TiO_2) thin films attract attention as a perspective construction material to be applied in different fields of advanced engineering technologies due to their unique properties. Titanium dioxide is an excellent material for many solid-state de-vices, i.e., sensors, solar cells, etc. [1, 2]. Having a high refraction index (n≈2.4), a large band gap (3.0 eV for rutile and 3.2 eV for anatase), the high thermal and chemical stability of properties the titanium oxide is widely used as films for multilayer optical filters [3], optical waveguides [4] and catalyst [5]. Furthermore, TiO_2 films have been considered as future candidates for a thin dielectric in dynamic random access memory storage capacitors [6–8].

Many techniques can be used to deposit TiO_2 films. They include solgel process [9], chemical vapor deposition [10], ion-assisted deposition [11], and sputtering [12]. Among these methods, reactive sputtering, one of the preferential methods, is characterized by the following features, which are attractive for industrial applications: (1) metal targets are used, (2) high deposition rate and (3) controllability of the film composition [13]. The properties of the titanium oxide films depend not only on the preparation techniques but also on the deposition conditions.

For this paper we used reactive magnetron sputtering method to fabricate TiO_2 thin films on different substrates. The dielectric and optical properties of the films as a function of the reactive sputtering process parameters were examined.

2. Experimental details

The schematics of experimental facility for deposition of titanium oxide films by reactive magnetron sputtering is shown in the fig. 1. The experimental facility was constructed on the basis of a vacuum unit VU-2MP. The vacuum chamber of the experimental facility was equipped with a magnetron sputtering system (MSS) and an ion source (IS) on the bases of a hall-current accelerator. The main feature of the MSS is the decrease of the working pressure down to 0.03 Pa that is achieved by using the magnetic system with an additional electromagnetic coil and the configuration of the magnetic field optimized on the target surface [14–16]. It gives a possibility to work at low gas flow (down to 50 sccm). Field strength at the target surface was 0.065 T.

The Ti target (VT1-0) ∅ 160 mm and thickness 10 mm has been sputtered by the method of magnetron sputtering in the Ar environment with a different content of the reactive gas (O_2). The O_2 content in the working gas mixture varied from 0 up to 50 % at the total chamber pressure of 0.05–0.06 Pa. Mass flow controllers RRG-1 were used for the control gas flow.

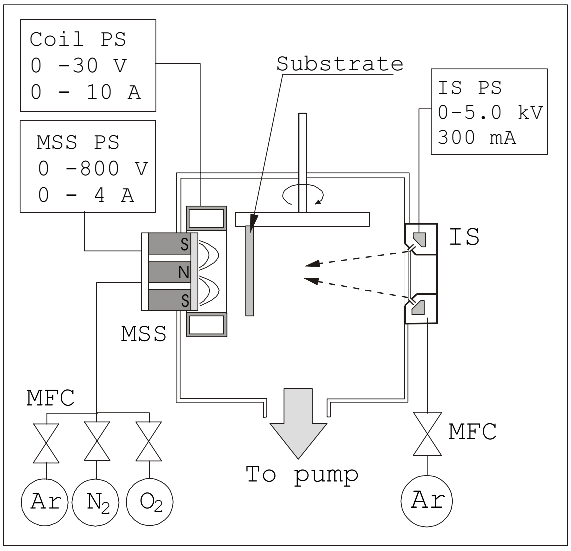

Fig. 1. Scheme of experimental facility for deposition of TiO_2 films by reactive magnetron sputtering method: IS – ion source; MSS – magnetron sputtering system; PS – power supply unit; MFC – mass flow control

The power supply source with the output power of 1.5 kW and ability of operation in the current or power stabilization mode was used for the MSS supply. To prevent an arc forming on the target surface the power supply was completed by an antiarc system.

The deposition of TiO_2 films was realized at discharge power 1.0 kW in a power stabilization mode. Thus the MSS discharge current and voltage were accordingly $I_t \approx 2.2$ A, $U_t \approx 450$ V.

Doped Si (100), optical glasses BK7 were used as substrates. The substrates were placed on a revolving type of substrate holder, and alternately brought to deposition zone. Substrates were placed at a distance of 11 cm from the MSS target surface.

The films were deposited up to thickness of 100–300 nm with the average deposition rate of 0.2–0.3 nm/s. Prior to start the deposition the substrates ion clearing was performed. Thus the ion source based on the hall-current accelerator was used. The vacuum chamber was pumped down to the base pressure of 10^{-3} Pa. Ar was fed into the IS up to the working pressure of $2.0\cdot10^{-2}$ Pa. The clearing time, ion energy and discharge current in all experiments were constant, and equal to 3 min, 700 eV, 40 mA accordingly.

The optical constants of deposited TiO_2 films (refraction index n, extinction coefficient k) on the wavelength of 0.63 μm were determined by the ellipsometry method by LEF-3M-1 ellipsometer under 65 in the light angle. Dispersions of the refraction index and the extinction coefficient in the waveband of 245–1650 nm was studied by spectroscopic ellipsometer M2000UI under 75° in the light angle of.

The permittivity and the dielectric loss tangent of films were determined on test structures. For this purpose the TiO_2 films were deposited on Si doped by boron up to the surface by 0.85–1.15 Ohm/□. The thickness of the deposited films, measured on the interference microscope MII-4, was about 100 nm. Then a Ni upper capacitor plate was deposited through a mask by magnetron sputtering on a TiO_2 film. The size of capacitors was 0.8×0.8 mm. Capacitor capacity and the dielectric loss tangent were measured by the digital RLC meter E7-8 (frequency 1.0 MHz). The values of permittivity were calculated according to the formula

$$\varepsilon = \frac{Cd}{\varepsilon_0 S},$$

where C – capacitor capacity, d – dielectric film thickness, ε_0 – dielectric constant $\varepsilon_0=8.85\cdot10^{-12}$ F/m, S – square of the capacitor.

3. Results and discussion

The dependence of MSS discharge voltage on reactive gas O_2 flow rate at sputtering Ti target at different pumping rate in magnetron discharge power stabilization mode (P=1.0 kW) were obtained. The flow rate of Ar to chamber was constant and equal to q_{Ar}=45 sccm. By changing the pumping system apertures the pumping rate D was varied. Depending on the pumping rate the chamber pressure was: D=1150 l/s, p=0.07 Pa; D=800 l/s, p=0.1 Pa; D=650 l/s, p=0.12 Pa.

It was determined, that the growth of the pumping rate leads to the increase of MSS discharge voltage and to the decrease in the voltage drop at transition from a metal to reactive mode and back (fig. 2). At high pumping speeds the transition to reactive mode of process was conducted at higher reactive gas flow rate, and the area of the magnetron discharge characteristics hysteresis considerably decreased, that allowed stabilizing the reactive magnetron sputtering process without application of special control systems.

The fig. 3 shows the dispersion of the refraction index of TiO_2 films deposited by the reactive magnetron sputtering method at different flow rate of the reactive gas O_2. The films were deposited in the power stabilization mode P_t=1.0 kW ($I_t \approx 2.2$ A) and at the target – substrate distance of 11 cm, Ar flow rate of 35 sccm, p=0.06 Pa. Deposition time is 10 min. On the spectral characteristic of the refraction index of TiO_2 films it is possible to select two fields: less than 800 nm, where n has a strong dependence on the wave-length and more than 800 nm, where n is practically independent on the wavelength. Spectral characteristics of the extinction coefficient have similar nature (fig. 4).

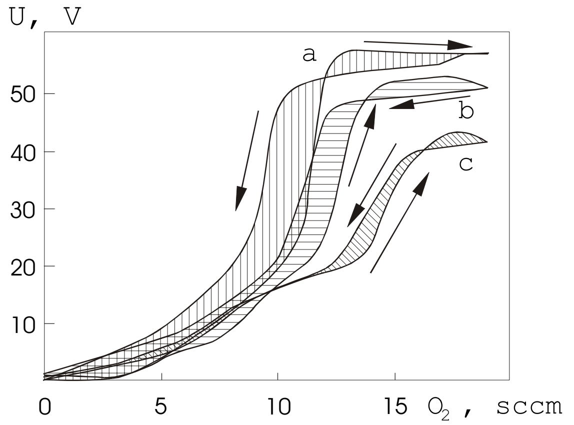

Fig. 2. Magnetron discharge voltage as a function of reactive gas O_2 flow rate at a sputtering Ti target in Ar/O_2 gases mixture at a different pumping rate: a – 650 l/s, b – 800 l/s, c – 1150 l/s. The minimal discharge voltage is accepted for zero

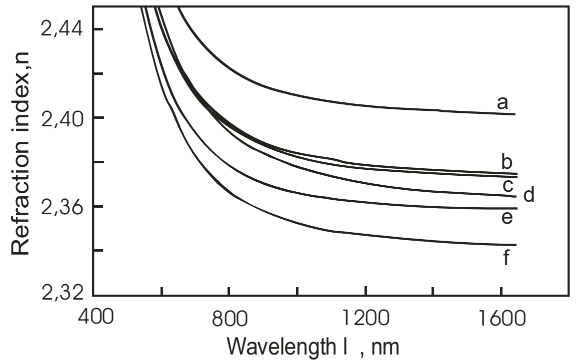

Fig. 3. Dispersion of refractive index of TiO_2 films at a different content of O_2 in mixture of working gases: a – 28.5 %, b – 26.0 %, c – 35.1 %, d – 23.7 %, e – 22.4 %, f – 38.0 %

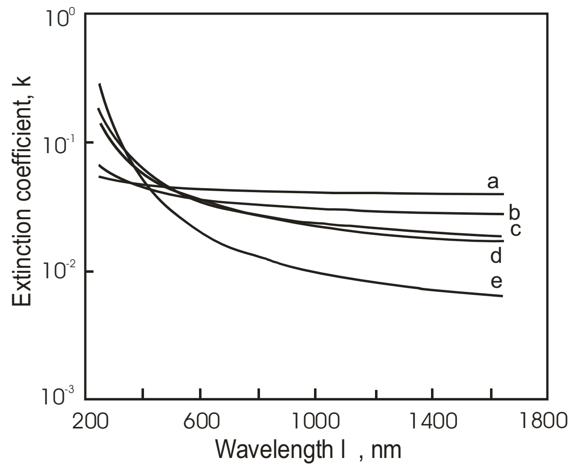

Fig. 4. Dispersion of extinction coefficient of TiO_2 films at a different content of O_2 in mixture of working gases: a – 22.4 %, b – 23.7 %, c – 38.7 %, d – 28.5 %, e – 26.0 %

Fig. 5 and fig. 6 show the dependences of refraction index and extinction coefficient on the wavelength of 630 nm on O_2 flow rate when depositing of TiO_2 films by reactive magnetron sputtering. Stoichiometric and close to stoichiometric films were obtained with more than 24 % of the content of oxygen in Ar/O_2 working gas mixture Thus the refraction index of films reached the value of 2.45. Close to a stoichiometric film had a rather low extinction coefficient (less than 0.05). It is necessary to notice, that on a wavelength 630 nm the refraction index is 2.67, and the extinction coefficient of a titanium is 3.72. The increase of oxygen concentration in the working gas mixture of more than 30 % led to a decrease in the refraction index and sharp increase of absorption of films.

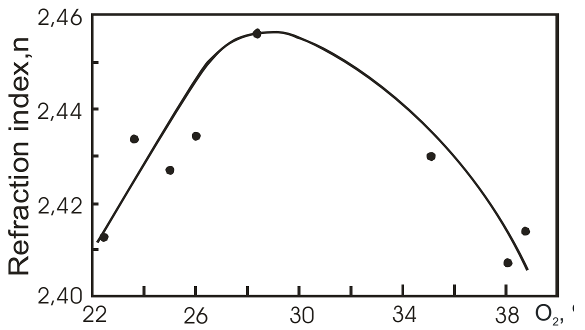

Fig. 5. Refraction index of TiO_2 films on a wavelength 0.63 μm as a function of oxygen concentration in Ar/O_2 gas mixture

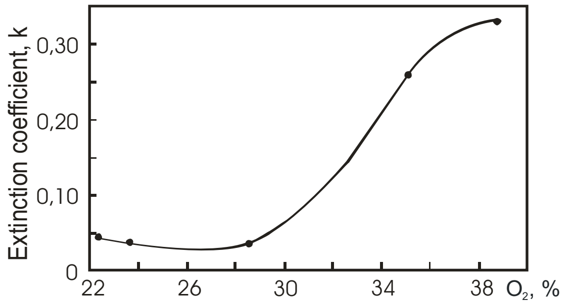

Fig. 6. Extinction coefficient on a wavelength 0.63 μm as a function of oxygen concentration in Ar/O_2 gas mixture

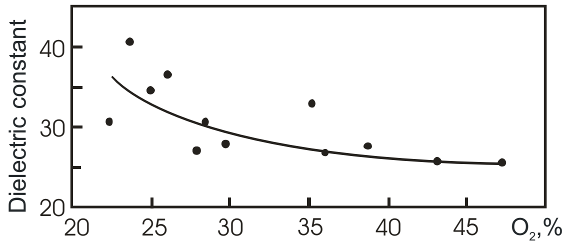

Fig. 7. Dependence of dielectric constant of TiO_2 films deposited by reactive magnetron sputtering method on content of oxygen in Ar/O_2 gas mixture

Fig. 7 and fig. 8 show the dependences of permittivity and dielectric loss tangent of titanium oxide films deposited by the reactive magnetron sputtering method on the oxygen content in mixture of working gases. TiO_2 films are obtained with the value of dielectric constant of ε=25–40 and loss angle of 0.01–0.02. It was determined, what at the content of oxygen about 23–27 % in the mixture of working gases titanium oxide films were obtained with the value of dielectric constant of 25–38 and loss angle of 0.01–0.012.

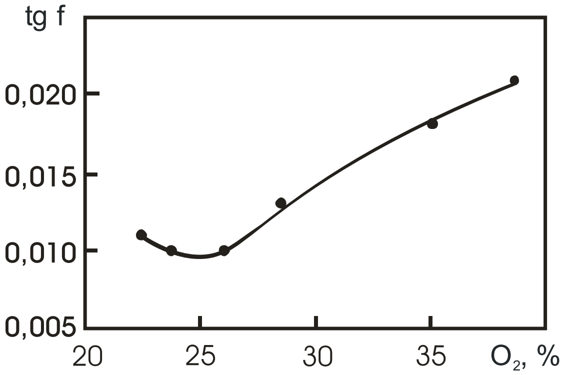

Fig. 8. Dependence of loss angle of TiO_2 films deposited by reactive magnetron sputtering method on content of oxygen in Ar/O_2 gas mixture

Conclusion

It was determined, that by the reactive magnetron sputtering method it is possible to create the repeatable deposition of titanium oxide films with refractive index of 2.34–2.38 and extinction coefficient of 0.006–0.02. TiO_2 films are obtained with the value of dielectric constant of 25–38 and loss angle of 0.01–0.02. These films may be used as optical coatings and dielectrics of condenser structure for integrated circuits.

References

[1] W.G. Lee, S.I. Woo, J.C. Kim, S.H. Choi, K.H. Oh, Thin Solid Films 237, 105 (1994).

[2] K.S. Yeung, Y.W. Lamb, Thin Solid Films 109, 242 (1993).

[3] Y. Sawada, Y. Taga, Thin Solid Films 116, 155 (1984).

[4] K.L. Siefering, G.L. Griffin, J. Electrochem. Soc. 137, 1206 (1990).

[5] K. Bange, C.R. Otterrnann, O. Anderson, U. Jeschkowski, M. Laube, R. Feile, Thin Solid Films 197, 279 (1991).

[6] N. Rausch, E.P. Burte, J. Electrochem. Soc. 140, 145 (1993).

[7] Y. Abe, T. Fukuda, Jpn. J. Appl. Phys. 33, 1248 (1994).

[8] Y.H. Lee, K.K. Chan, M.J. Brady, J. Vac. Sci. Technol. A 13, 596 (1995).

[9] C. Yu. Jimmy, Jiaguo Yu, Jincai Zhao, Applied catalysis B 36, 31 (2002).

[10] J.P. Lu, J. Wang, R. Raj, Thin Solid Films 204, L13 (1991).

[11] S. Miyaki, T. Kobayashi, M. Satou, F. Fijimoto, J. Vac. Sci. Technol. A 9, 3036 (1991).

[12] Diana Mardare, Peter Hones, Mater.Sci.Engg. B 68, 42 (1999).

[13] T. Ohwaki, Y. Taga, Appl. Phys. Lett. 54/17, 1664 (1989).

[14] I.V. Svadkovski, D.A. Golosov, S.M. Zavatskiy, Vacuum 68/4, 283 (2003).

[15] D.A. Golosov, I.V. Svadkovskii, S.M. Zavadskii, Surf. Eng. and Appl. Electrochem. 6, 56 (2002).

[16] D.A. Golosov, I.V. Svadkovski, S.M. Zavadski, *in Proc. VI Int. Conf. Modif. of Mater. by particle beams and plasma flows*, Tomsk, 2002, 148–150.