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# Micro-structural and dielectric properties of porous $TiO_2$ films synthesized on titanium alloys by micro-arc discharge oxidization

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## Abstract

Titanium oxide ($TiO_2$) has stable dielectric properties characterized by a high relative dielectric constant and low dielectric loss, and the materials have attracted much attention in microelectronics and microwave applications. In this work, the dielectric properties of porous $TiO_2$ films formed on TC11 titanium alloys by micro-arc discharge oxidization (MDO) using different current densities were investigated. The micro-structures, compositions, and dielectric constant of the films were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), and vector analysis. The growth rates, composition phases, and properties of the pores in the films are found to strongly depend on the electrical current density. The acquired complex permittivity values are correlated to the structural and compositional changes. At a frequency of 10.80 GHz, the dielectric constants of the film with a thickness of approximately 10 μm prepared under different current densities of 18, 12 and 6 A dm$^{-2}$ were 12.20, 14.61, and 16.91, respectively, and the tangential losses were $1.1 \times 10^{-2}$, $1.3 \times 10^{-2}$, and $1.4 \times 10^{-2}$, respectively. The relationship between the dielectric properties of the MDO $TiO_2$ with the structure and composition is discussed.

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*Keywords:* Micro-arc discharge oxidization; Porous $TiO_2$ films; Dielectric constant

## 1. Introduction

Titanium oxide ($TiO_2$) thin films have recently attracted much attention due to their potential applications in microelectronic devices and microwave communication systems. The materials possess stable dielectric properties characterized by a high relative dielectric constant and low dielectric loss [1,2]. Many deposition methods have been used to prepare $TiO_2$ films including pulsed laser deposition [3], filtered arc deposition [4], sol–gel method [5], and reactive sputtering methods [6]. Recently, micro-arc discharge oxidization (MDO) has been developed to produce ceramic overcoats on titanium substrates [7]. By applying discharges at a high voltage, porous $TiO_2$ films including the three polymorphic forms, rutile, anatase, and brookite, can be formed on titanium and its alloy. Insulating films with the desired properties can be fabricated using this method. Previous reports on $TiO_2$ films prepared by MDO have primarily focused on the surface mechanical and biological properties of the materials whereas there have been few reports on their dielectric properties which are important in many applications [7–13]. In the present work, the dielectric properties of porous $TiO_2$ films synthesized on titanium alloys by MDO employing different current densities were evaluated and the relationship between the dielectric properties with the structure and composition of the materials were studied.

## 2. Experimental details

Rectangular disks (45 mm × 45 mm × 2 mm) made of TC11 titanium alloy (composition: Al = 5.8–7.0, Mo = 2.8–3.8, Zr = 0.8–2.0, Si = 0.2–0.35, Fe = 0.25, other elements = 0.4) were used in our experiments. After polishing and cleaning with acetone and distilled water, the specimens underwent MDO in an aqueous solution of electrolytes that were prepared using pure $NaWO_3$, $Na_3PO_4 \cdot 12H_2O$. The treatment apparatus consisted of a stainless steel bath and pulse voltage power supply as shown in Fig. 1. The applied voltage was varied from 350 to 450 V, the frequency was 1.25 kHz, and the pulse width was 300 μs. During the process, a constant average current density was maintained on the sample surface by controlling the voltage. The electrolyte temperature was less than 50 °C.

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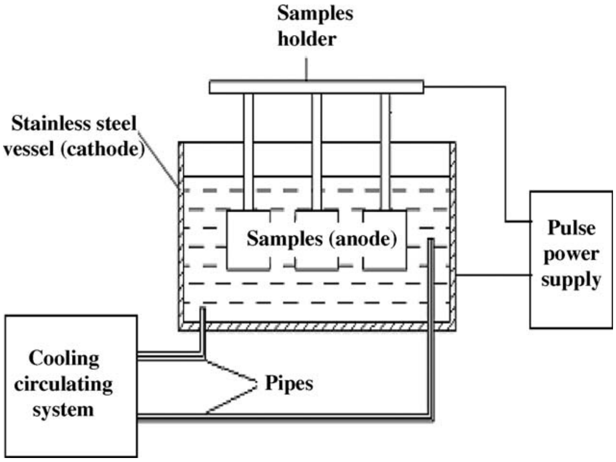

Fig. 1. Schematic of the MDO apparatus.

X-ray diffraction (XRD) spectra of the films were acquired using the Cu Kα line with a step of 0.05° in a standard X-ray diffraction. The surface morphology of the films was observed using scanning electron microscopy (SEM). The thickness of the film was obtained by an eddy current thickness meter. The real and imaginary permittivity parts of the $TiO_2$ film were determined at a frequency of 10.80 GHz by the *S*-parameter Model. The *S*-parameters were measured by a network analyzer HP8718D and programmed by a Through Reflect Line (TRL) calibration kit.

## 3. Results and discussion

Fig. 2 shows that the growth rate increases with current densities. The SEM pictures acquired from MDO $TiO_2$ films with the same thickness of 10 μm fabricated using three different current densities of 6, 12, and 18 A $dm^{-2}$ are displayed in Fig. 3. It can be observed that pores with a maximum diameter of several micrometers are randomly distributed on the surface, and the maximal pore diameter is observed to increase with the current density. The plasma discharges on the samples are more intense during MDO with increasing average current densities for the same electrolyte composition, applied voltage frequency, and pulse width [7]. When a micro-arc discharge extinguishes in the discharge channel, coarse pores with larger diameters may be left on the coating surface.

The phases of the MAO $TiO_2$ films are characterized by XRD, and the results are shown in Fig. 4. It can be seen that all the films are composed of rutile and anatase $TiO_2$, and no other crystalline phases are detected. When the current density goes up, the intensity of the rutile phase increases.

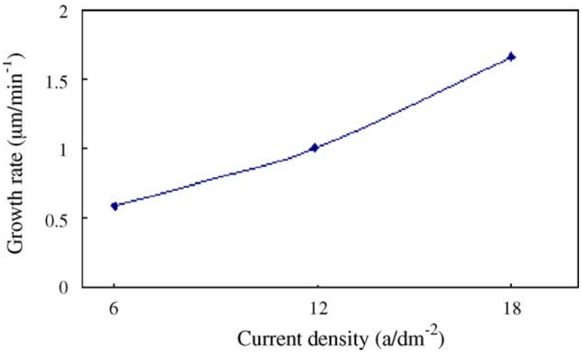

Fig. 2. MDO $TiO_2$ film growth rates as a function of current densities.

Development of novel materials with high relative permittivity values ($\varepsilon_r'$), low current losses ($\varepsilon_r''$), and low $\tan\delta$ ($\tan\delta \equiv \delta_r''/\delta_r'$) at high frequencies are being actively pursued. In this work, the permittivity of MDO $TiO_2$ films with respect to the relative dielectric constant ($\varepsilon_r'$) and tangential loss ($\tan\delta$) is determined at 10.80 GHz. The relative dielectric constant ($\varepsilon_r'$) and

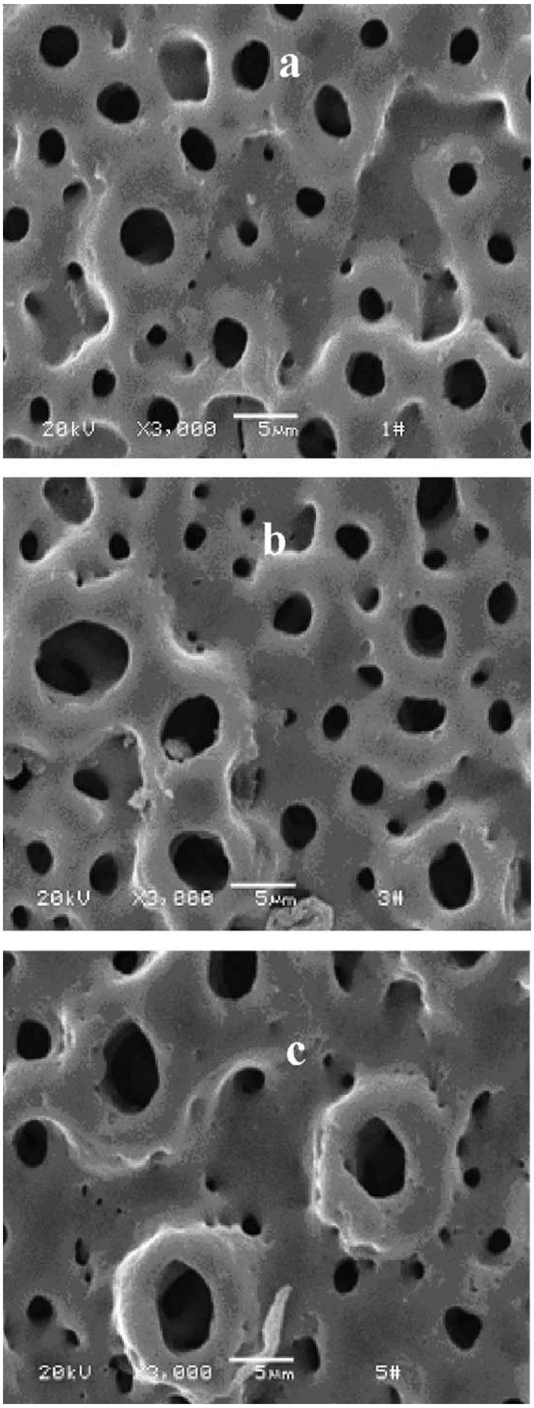

Fig. 3. SEM micrographs of MDO $TiO_2$ films fabricated using different current densities: (a) 6 A $dm^{-2}$, (b) 12 A $dm^{-2}$, and (c) 18 A $dm^{-2}$.

Table 1
Microwave dielectric properties of MDO $TiO_2$ films fabricated using different current densities

| Film thickness (μm) | $f_0$ (GHz) | Current density ($A\,dm^{-2}$) | Relative dielectric constant ($\varepsilon$) | tan $\delta$ |
|---|---|---|---|---|
| 10 | 10.80 | 6 | 16.91 | $1.4 \times 10^{-2}$ |
| 10 | 10.80 | 12 | 14.61 | $1.3 \times 10^{-2}$ |
| 10 | 10.80 | 18 | 12.20 | $1.1 \times 10^{-2}$ |

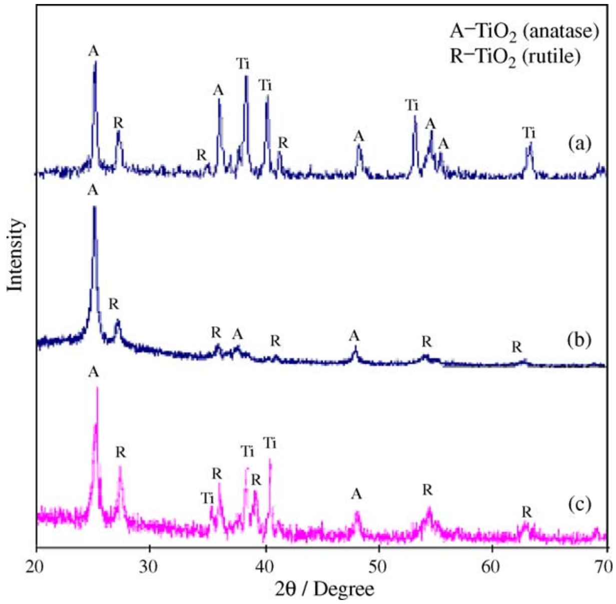

Fig. 4. X-ray diffraction patterns of MDO $TiO_2$ films produced using different current densities: (a) 6 $A\,dm^{-2}$, (b) 12 $A\,dm^{-2}$, (c) 18 $A\,dm^{-2}$.

tangential loss (tan $\delta$) of the MDO $TiO_2$ films with a thickness of 10 μm formed at different current densities of 6, 12, and 18 $A\,dm^{-2}$ are shown in Table 1.

The dielectric constants and tangential losses are observed to vary. Both of them decrease with increasing current density. This observation is in line with that predicted by the effective dielectric constant theory [14]. The effective dielectric constant $\varepsilon_p$ of the isotropic porous materials can be evaluated by splitting the volume of the materials into portions with different dielectric constants and performing integration as follows:

$$\varepsilon_p = \frac{1}{v}\int \varepsilon\, dv \qquad (1)$$

where $v$ is the volume of the materials and $\varepsilon$ the dielectric constant of the medium with a volume of $dv$. For the porous $TiO_2$ films composed of the anatase and rutile phases, $f$ is the porosity, $v_r$ the volume of rutile $TiO_2$, and $v_a$ is the volume of anatase $TiO_2$. Using the dielectric constants of $TiO_2$ with anatase ($\varepsilon_a$) and rutile ($\varepsilon_r$) phases respectively and the relative permittivity of air being 1, we have

$$\varepsilon_p = f + (1-f)\varepsilon = f + v_r\varepsilon_r + v_a\varepsilon_a \qquad (2)$$

Eq. (2) shows that $\varepsilon_p$ is a decreasing function of $f$. Based on the structure and composition of the films prepared by MDO using different current densities, the porosity $f$ varies with the current densities as well as composition. This is confirmed by our experimental results showing that the current density inevitably changes the dielectric constant of the materials. It is thus an important parameter in the fabrication process.

## 4. Conclusion

Porous $TiO_2$ films composed of anatase and rutile phases are formed on TC11 titanium by MDO using different current densities. The growth rate and maximal pore size are observed to increase with current density, and so is the intensity of the rutile phase. The dielectric constants of the films fabricated using different current densities are different. For MDO $TiO_2$ films with a thickness of 10 μm prepared at current densities of 18, 12 and 6 $A\,dm^{-2}$, the dielectric constants are 12.20, 14.61 and 16.91, respectively. The dielectric constants of the porous MDO $TiO_2$ films depend on the structure and composition, and it can be evaluated by the effective dielectric constant theory. Changing the parameters during MDO, $TiO_2$ films with various dielectric constants can be obtained to satisfy specific needs by different applications.

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