Structural and dielectric properties of TiO$_2$ thin films deposited by the sol-gel method on Si substrates

P Vitanov, A Harizanova and T Ivanova

Central Laboratory for Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72, Tsarigradsko Chaussee, 1784 Sofia, Bulgaria

E-mail: tativan@phys.bas.bg

Abstract. Titanium dioxide thin films with good dielectric properties were obtained on Si substrates using the sol-gel method. The metal oxide films were deposited by spin coating from sol solution and additionally annealed at 600 °C and 850 °C. XRD analysis, FTIR and Raman spectroscopy were used for revealing the film structure, the crystal phases and the formation of a polycrystalline material. The electrical measurements on metal-insulator-silicon (MIS) structures showed good dielectric properties. An optimal regime for high temperature annealing (850°C/15 min) was found, for which no effects related to the thermal instability of TiO$_2$ film on Si were observed. The leakage current density of a 38-nm thick TiO$_2$ film annealed at 850°C/15 min/O$_2$ was approximately 1.95×10$^{-9}$ A/cm$^2$ at 1.6×10$^{-6}$ V/cm.

1. Introduction

Titanium dioxide has been recognized as one of the most important materials for applications in the semiconductor electrochemistry, as a gas sensor [1], as antireflective coatings [2], in electrochromic devices and solar cells [3], as photocatalysts and optical filters [4]. TiO$_2$ is also used as a dielectric material for electronic devices [5].

The TiO$_2$-Si system has been intensively studied for high-$k$ applications in memory capacitors and in nanoscale MOSFET [3, 6]. It is attractive as it has high permittivity $k = 80$-110 depending on the crystal structure and the method of deposition [7]. TiO$_2$ crystallizes at temperatures above 400°C, therefore it is expected to exhibit a polycrystalline morphology. In many cases, the polycrystalline structure might be problematic due to the grain boundaries acting as high leakage paths. In order to address this issue, lanthanide dopants in TiO$_x$ films are utilized to create and maintain an amorphous phase for capacitor applications [8]. Another approach is to use pseudobinary alloys [9]. It is important to note that TiO$_2$ is not thermodynamically stable on Si during deposition by CVD and other technological processes [10]. When TiO$_2$ films are obtained by different methods and undergo various types of annealings, TiO$_2$ may react with the Si surface to form Ti–O–Si bonds. This leads to a decrease of the maximum capacitance of metal-insulator-silicon (MIS) structures as a result of the decrease of the effective dielectric constant.

Recently, sol-gel technology has been intensively developed to synthesize various functional coating films. This process possesses many advantages, such as the utilization of simple equipment, high homogeneity of the films deposited and the possibility to use a great variety of substrates and
sizes [11]. It is used with a low temperature treatment that has the potential to prevent the TiO₂/Si reaction and produce high-quality MIS structures.

The purpose of this work is to show that the sol-gel method allows one to prepare thin TiO₂ films on Si with good quality. Thin TiO₂ thin films were deposited by spin coating. The structural properties as a function of the annealing temperature were studied by XRD and Raman and FTIR spectroscopy. The electric properties of TiO₂ films were investigated using MIS structures.

2. Experimental details

The TiO₂ layers were prepared by the sol-gel technology. Titanium ethoxide (TEOT) (Fluka type) was used as a precursor. The introduction of glacial acetic acid (Fluka type), with molar ratio TEOT:acetic acid 1:1.5 caused acetate modification, resulting in an exothermic reaction. Further, the solution was modified by 60 moles of water. This led to hydrolysis and condensation reactions, resulting into the gel formation. Acetylacetone acts as a peptizing agent and stabilizer and is added in a molar ratio TEOT:acetylacetone 1:1. More details about titanium sol formation can be found in [12].

The films were deposited by spin coating at 8000 rpm for 30 sec. The annealing procedures of the films consisted of low temperature firing at 350 °C for 30 min and two high-temperature treatments at 600 °C for 60 min and at 850 °C for 15 min. The film thickness was measured with a laser ellipsometer at the wavelength of 632.8 nm. The film thickness is 38 nm. The films obtained are dense, homogenous and smooth with good thickness uniformity of ± 1% across the wafer.

The starting material was a polished p-type Si wafer, with orientation <100> and resistivity of 7 Ω.cm. The substrates were carefully cleaned ultrasonically in acetone and ethanol for 5 min. The second step was etching in 10 % HF solution followed by placing the wafers H₂SO₄:H₂O₂ = 1:1 solution (80 °C) for 60 min. This treatment leads to the formation of chemical SiO₂ with thickness of 1-2 nm. This initial oxide is used to create an interfacial layer between the Si wafer and the deposited film. Finally, the wafers were cleaned in deionized water in an ultrasonic bath for 10 min (60 °C).

The crystallization behavior of the TiO₂ film was studied by X-Ray diffraction (at grazing incidence angle of 7°). The Raman scattering spectra were measured by a double spectrometer SPEX 403 with a photomultiplier detector. The FTIR measurements were performed by Shimadzu FTIR Spectrophotometer IRPrestige-21.

The electrical properties of the layers were studied using MIS structures. Aluminium was evaporated on the backside of the Si and a Hg probe was used as an upper electrode. The MIS structures were formed using TiO₂ films annealed at different temperatures – 600 °C (60 min) and 850 °C (15 min).

3. Results and discussions

The X-ray diffraction (XRD) pattern recorded at the grazing incidence angle of 7° shows that the metal oxide layer annealed at 850 °C has a polycrystalline structure corresponding to the rutile phase (see figure 1). The line at 2θ = 33.6° is due to the Si substrate. The strongest peak at 27.5° corresponds to the main XRD line of a rutile phase (110) (JCPDS card 21-1276). The rutile phase is manifested also by additional less intense peaks. Only one weak XRD maximum at 2θ = 25.3° can be assigned to an anatase modification (JCPDS card 21-1272).

The percentage of the rutile phase in the film structure can be estimated from the respective integrated XRD peak intensities using the equation

\[ I = \frac{K}{d^2} \cos^2 \theta \]

where

- \( I \) is the peak intensity,
- \( K \) is a constant,
- \( d \) is the interplanar spacing,
- \( \theta \) is the diffraction angle.

The percentage of the rutile phase can be determined by comparing the integrated peak intensities of the (110) rutile and (101) anatase peaks.

![Figure 1. XRD spectrum of a TiO₂ film annealed at 850 °C in oxygen for 15 min.](image-url)
given in ref [13], considering the anatase peak (101) and the strongest rutile (110) peak. The value obtained is 82 % of rutile phase and, respectively, 18 % anatase titanium dioxide. Based on the XRD data, the lattice parameters are determined as \( a = 4.583 \) Å and \( c = 2.989 \) Å. They are very close to the standard ones \( (a = 4.5933 \) Å, \( c = 2.9592 \) Å, JCPDS card 21-1276). The short high-temperature annealing at 850 °C causes the film to crystallize into a thermodynamically stable rutile phase, despite the metastable anatase structure. Such thermal behavior has been observed by other authors [14].

The structural transformation of TiO\(_2\) films deposited on Si was studied by two other characterization techniques as a function of the annealing temperatures. Both FTIR and Raman spectroscopy can reveal the crystalline phases existing in the thin film structure.

FTIR spectra of the films are shown in figure 2. The TiO\(_2\) film annealed at the lower temperature (600 °C) exhibits two absorption bands. The strong line at 437.8 cm\(^{-1}\) is assigned to Ti-O bonding in crystalline anatase TiO\(_2\), very close to the value (435 cm\(^{-1}\)) of anatase crystal [15]. The band at 653.7 cm\(^{-1}\) is attributed to Ti-O stretching vibrations.

The thermal treatment at 850 °C leads to the appearance of more IR lines. The absorption lines located at 376.1, 445.6, 495.7 cm\(^{-1}\) and at 810 cm\(^{-1}\) are referred to a rutile phase [16]. The 673.2 cm\(^{-1}\) band is due to the Ti-O stretching mode. The existence of the absorption band at 1070 cm\(^{-1}\) is a sign of Ti-O-Si bonding and penetration of Si into the film [17]. The FTIR analysis confirms the XRD results, namely, that the short treatment at 850 °C causes crystallization in a rutile phase and the TiO\(_2\) film annealed at 600 °C shows the presence of an anatase phase. These results were confirmed by the Raman study as well.

The effect of the two annealing temperatures was also studied by Raman spectroscopy (Fig. 3). The common Raman lines appearing in the two spectra are due to the Si substrate. The strong peak at 520 cm\(^{-1}\) is related to the phonon vibrations of Si, while the other Si peaks are located at 305 cm\(^{-1}\) and 960 cm\(^{-1}\). The TiO\(_2\) films annealed at the lower temperature, 600 °C, revealed Raman peaks at 144, 197, 398 and 635 cm\(^{-1}\). The well-defined line at 144 cm\(^{-1}\) is attributed to the anatase phase. This peak is reported to be a very sensitive feature for anatase [18]. The small shoulder at 197 cm\(^{-1}\) and the lines at 398 and 635 cm\(^{-1}\) are due to anatase as they have been found in the Raman spectrum of anatase single crystal [18]. Meanwhile, increasing the annealing temperature leads to the disappearance of the strong peak at 144 cm\(^{-1}\), while new lines at 230, 444 and 612 cm\(^{-1}\) are detected. They are assigned only to rutile TiO\(_2\); their positions coincide with the literature data [19]. This suggests that the annealing at 600 °C/60 min results in an anatase crystalline structure, while annealing at 850 °C/15 min induces the film crystallization in a rutile phase. This conclusion is in good agreement with the XRD and FTIR studies.
We also measured the high-frequency (1 MHz) and the quasistatic-pulsed C-V characteristics of MIS structures. As a comparison, Table 1 presents the results for the dielectric properties of TiO$_2$ films annealed at 600 °C (60 min) and 850 °C (15 min). The dielectric constant of TiO$_2$ films as determined from the quasistatic CV measurements slightly decreases as the annealing temperature is increased. The leakage current density also decreases when the annealing temperature is raised.

Table 1. The results of measurements of MIS structures with TiO$_2$ thin film.

| Annealing conditions | Dielectric constant at 1 MHz | Dielectric constant from quasi-static C-V tests | Density of fixed charge $N_f$ [cm$^{-2}$] | Lowest surface state density $D_{it}$ [eV$^{-1}$cm$^{-2}$] |
|----------------------|----------------------------|-----------------------------------------------|------------------------------------------|---------------------------------------------|
| 600 °C/60 min/air    | 20.0                       | 24.0                                          | $-8.26 \times 10^{10}$                    | $1.1 \times 10^{12}$                        |
| 850 °C/15 min/air    | 20.4                       | 20.4                                          | $-6.55 \times 10^{11}$                    | $2.4 \times 10^{11}$                        |

Conclusions
The sol-gel approach proposed and the spinning procedure result in the formation of thin films (below 100 nm) of TiO$_2$ on Si substrates with good dielectric properties. The main properties were investigated of MIS structures fabricated by this method. An optimal regime for high temperature annealing (850 °C/15 min) was found, for which no effects related to the thermal instability of TiO$_2$ film on Si were observed. The results obtained show that this deposition method can find applications in the semiconductor technology.

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