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Thin Solid Films xx (2005) xxx - xxx



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Structural and electrical characterization of TiO₂ films grown by spray pyrolysis

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Abstract

The sol-gel spray pyrolysis method was used to grow TiO₂ thin films onto silicon wafers at substrate temperatures between 315 and 500 °C using pulsed spray solution feed followed by annealing in the temperature interval from 500 to 800 °C in air. According to FTIR, XRD, and Raman, the anatase/rutile phase transformation temperature was found to depend on the film deposition temperature. Film thickness and refractive index were determined by Ellipsometry, giving the refractive indexes of 2.1–2.3 and 2.2–2.6 for anatase and rutile, respectively. According to AFM, film roughness increases with annealing temperature from 700 to 800 °C from 0.60 to 1.10 nm and from 0.35 to 0.70 nm for the films deposited at 375 and 435 °C, respectively. The effective dielectric constant values were in the range of 36 to 46 for anatase and 53 to 70 for rutile at 10 kHz. The conductivity activation energy for TiO₂ films with anatase and rutile structure was found to be 100 and 60 meV, respectively. © 2005 Elsevier B.V. All rights reserved.

PACS: 01.03.Cc Keywords: TiO₂; Spray pyrolysis; Structure; Electrical properties

1. Introduction

TiO₂ films prepared by spray pyrolysis have attracted growing interest due to their wide range of applications such as electrodes for solar cells [1], photocatalyst [2] and gas sensor devices [3]. Only in few works the formation and composition of sol-gel spray pyrolysis deposited TiO₂ films from acetylacetone stabilized Ti-alkoxide precursors have been studied [3-5]. In our previous work we showed that the substrate temperature has a large effect on the structure of sprayed TiO₂ films [5]. The thermoanalytical study of the acetylacetonate stabilized Ti-isopropoxide showed the formation of TiO₂ anatase phase at 500 °C and TiO₂ rutile phase at 800 °C [6]. Mainly, Raman and/or IR-spectroscopy have been applied to characterize the structural properties of sol-gel TiO₂ powders [7–9], and films [5,10–13]. Electrical properties of sol-gel processed TiO₂ films have been studied only in few works [3,5,13].

To our knowledge no systematic study on preparation conditions in connection with structural and electrical characterization of the TiO_2 films deposited by sol-gel spray pyrolysis technique from the system of acetylacetonate stabilized Ti-isopropoxide has been performed.

The aim of this paper is to report on the spray-pyrolysis processing, structure, optical and electrical properties of TiO_2 thin films as a function of deposition and annealing temperatures.

2. Experimental details

The precursor solution contained titanium(IV)isopropoxide (TTIP), acetylacetone (AcAc) and ethanol with TTIP concentration of 6 vol.% at TTIP:AcAc molar ratio of 1:2. The solution was atomized by a pneumatic spray system using compressed air as a carrier gas onto Si (100) (ρ =1.0-30.0 Ω cm) and HD (high density) Si (100) (ρ =0.001-0.005 Ω cm) wafers. The films were deposited at 300-500 °C by a pulsed solution feed. The pulse consists of one minute of spray time and one minute of pause; up to three pulses were performed. The films were subsequently

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Fig. 1. Raman spectra of TiO₂ films deposited at different temperatures (T_s) and annealed (T_a) at 700 and 800 °C.

heat treated for 15 min at 500 $^{\circ}\mathrm{C}$ followed by 30 min at 700 and 800 $^{\circ}\mathrm{C}$ in air.

XRD patterns were recorded by a Bruker AXS D5005 diffractometer using Cu–K α radiation (λ =1.542 Å). FTIR transmittance spectra of the films on Si (100) wafers were measured in the spectrum region of $4000-400 \text{ cm}^{-1}$ on a Perkin Elmer GX-1 spectrometer. Raman spectroscopy was performed at room temperature with the excitation wavelength of 532 nm and output power of 2 mW by means of the Raman setup with the Spex 340E monochromator. Ellipsometric investigations were conducted on a high precision DRE ELX-02C ellipsometer equipped with a He–Ne laser source (λ =632.8 nm). AFM images were obtained using NT-MDT scanning head Smena and MicroMasch cantilevers CSC 21 with silicon probe tip in contact mode. The films roughness was characterized by the image based Root Mean Square (RMS) roughness calculated over the whole scanned surface images using a Scanning Probe Image Processor SPIP V3.2.4.0. The electrical properties of TiO₂ films on HD Si (100) substrates were assessed by a computer controlled Agilent 4192A impedance analyzer in the temperature interval of 20-120 °C. Sputtered Au electrodes with the area of $2.88 \cdot 10^{-7}$ m² were applied for front contact. The bottom contact was established by scratching a corner of the film and applying a high conductive silver paste.

3. Results and discussion

3.1. Structural study

Deposition of TiO₂ films at temperatures below 435 °C result in amorphous films, according to XRD. FTIR results, however, indicate the Ti–O–Ti vibrations characteristic for the TiO₂–anatase [5]. Subsequent annealing at 500 °C in air leads to the carbon-free TiO₂–anatase films with low crystallinity [5]. Raman results for as-deposited and for films annealed at 500 °C (spectra are not presented) are in accordance with the XRD study presented in our previous work [5].

Upon annealing at 700 °C the films grown at temperatures 315-435 °C show Raman peaks at 148, 200, 399 and 641 cm⁻¹, belonging to the E_g , E_g , B_{1g} , E_g , anatase modes, respectively [14]. Fig. 1 shows the Raman spectra of TiO₂ films deposited at 375 and 435 °C. The relative intensities of the Raman peaks at 148 and 399 cm^{-1} were used to determine the relative amount of anatase in TiO₂ films. The ratio is found to depend on the film growth temperature indicating the highest value for the film deposited at 315 °C (Spectrum is not shown). The ratio of anatase peak intensities is observed to decrease for the film deposited at 435 °C. This effect can be explained by the arising amount of rutile as indicated by IR spectra where the absorption peak at 496 cm⁻¹, characteristic for the TiO_2 -rutile [3] is detected in an addition to the TiO_2 -anatase peak at 436 cm⁻¹ [5]. Raman spectrum of the film grown at 500 °C and annealed at 700 °C (spectrum is not shown) clearly shows the peaks at 442 and 617 cm⁻¹, characteristic for the TiO₂ rutile modes [7]. Raman results of the films annealed at 700 °C correspond to the ones obtained by XRD and FTIR presented in our earlier work [5].

Upon annealing at 800 °C the films deposited below 400 °C and above 400 °C remain anatase and rutile, respectively (Fig. 1). The spectra associated for the films deposited below 400 °C indicate the narrowing of the bands and the shift in the peak positions (Fig. 1). After the heat-treatment at 800 °C the main anatase peak at 148 cm⁻¹, characteristic for the films annealed at 700 °C, shifts to 144 cm⁻¹. Similar shift was observed for the TiO₂ nanophase samples annealed in air [9]. The full width at half maximum (FWHM) of the main anatase peak of the films grown below 400 °C decreases with increasing the annealing temperature (from 700 to 800 °C) from 17 ± 0.7 to 14 ± 0.7 cm⁻¹, indicating the structural improvement. For comparison, FWHM of 25.5 and 11 cm⁻¹ were found for a nanophase TiO₂ and epitaxially grown TiO₂ films, respectively [9].

IR spectrum of the film deposited at 435 °C and subjected to annealing at 800 °C, shows the absorption at 496 cm⁻¹ characteristic for rutile, whereas a weak response of anatase at 436 cm⁻¹ could be still observed (figure not shown). Raman (Fig. 1) and XRD (figure not shown) studies indicate that rutile is the crystalline phase in this sample. The structural development of TiO₂ films deposited at different substrate temperatures and subjected to annealing at 700 and 800 °C is summarised in Table 1.

Table 1.

Summary on structural study by FTIR, Raman and XRD techniques of TiO_2 films deposited by sol-gel method at different deposition temperatures (T_s) and subjected to post-deposition annealing (T_a) for 30 min at 700 and 800 °C in air

<i>T</i> _s (°C)	$T_{\rm a}$ =700 °C			<i>T</i> _a =800 °C		
	FTIR	Raman	XRD	FTIR	Raman	XRD
<400	А	А	А	А	А	А
435	A+R	А	А	R+(A)	R	R
500	R	R	R	R	R	R

A-anatase, B-rutile.

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Z (nm) 5.0

0.0

5.0

5.0

a)

Z (nm)

Fig. 2. AFM images of TiO₂ films deposited by spray at 435 °C and annealed (a) at 700 and (b) at 800 °C.

The (101) peak of anatase and the (110) peak of rutile phases on the XRD patterns were used to calculate the mean crystallite size by the Scherrer formula. The mean crystallite size increases with the annealing temperature (from 700 to 800 °C) from 30 to 59 nm for TiO₂-anatase films (T_s < 400 °C) and from 50 to 86 nm for TiO₂-rutile films (T_s > 400 °C).

Raman, IR-spectroscopy and XRD results indicate that TiO_2 films deposited at substrate temperatures of 315 and 375 °C remain anatase even after annealing at 800 °C. The films grown at 435 °C show crystalline anatase structure after annealing at 700 °C which turns to crystalline rutile by annealing at 800 °C. However, at both annealing temperatures a mixture of anatase and rutile phases were present according to the IR spectra. The deposition at 500 °C followed by the annealing at 700 °C and at higher temperatures result in TiO_2 rutile phase.

3.2. Ellipsometric characterization and morphology

TiO₂ film thicknesses are rising with the growth temperature as determined by Ellipsometric measurements. After annealing at 700 °C the films deposited using one spray pulse show the thickness of 60, 90, 100 and 120 nm at substrate temperatures of 315, 375, 435 and 500 °C, respectively. The film thickness depends on the number of spray pulses almost linearly.

The refractive index of TiO_2 -anatase films increases from 2.1 up to 2.3 if annealing temperature rises from 700 up to 800 °C indicating the film densification. A lowering in the film thickness accompanied by the increase in the film refractive index (from 2.2 up to 2.6) has been observed if the annealing temperature for the film deposited at 435 °C is changed from 700 to 800 °C. Such behaviour is in correspondence with the structural changes (anatase-rutile at 700 °C, rutile at 800 °C, see Section 3.1).

In addition, the annealing at 700 °C promotes the growth of an interfacial SiO₂ layer at Si/TiO₂ interface confirmed by the absorption around 1060 cm⁻¹ in FTIR spectra, shown in our previous study [5]. According to the Ellipsometric measurements the thickness of SiO₂ layer increases from the average of 5 to 10–20 nm by annealing at 700 and 800 °C, respectively. The presence of the SiO₂ layer is taken into account in electrical characterization of the films (see Section 3.3).

The surface roughness of the films deposited below 500 °C increases about twice with the increase of the annealing temperature from 700 to 800 °C as detected by AFM. The image based root mean square roughness (RMS) for the TiO_2 films deposited at 375 °C is 0.6 and 1.1 nm after the annealing at 700 and 800 °C, respectively. For the films deposited at 435 °C the RMS roughness is detected to be 0.35 and 0.70 nm after annealing at 700 and 800 °C, respectively (Fig. 2). The increase of the surface roughness with annealing temperature could be caused by the growth of the crystallite size as shown by XRD studies. The increase of the samples deposited at 500 °C.

3.3. Electrical characterization

Frequency and temperature dependent impedance properties at zero bias voltage were investigated for the annealed films with anatase and rutile structure (see Table 1). The variation of the loss tangent $(\tan \delta)$ with frequency for TiO₂ film with anatase structure (deposited at 315 °C and annealed at 700 °C) shows a shift of the well-resolved maximum at temperatures higher than 80 °C (Fig. 3). The measurements of the dissipation factor as a function of temperature enables to calculate the activation energy of relaxation (E_a) by taking the frequency of the dielectric loss peak vs. temperature and using the Arrhenius relation [15]. The activation energy of dielectric relaxation, shown in Fig. 3, ranges from 0.70 to 0.78 eV.



Fig. 3. Dielectric loss (tan δ) vs. frequency (T_s =315 °C, T_{an} =700 °C), and frequency of dielectric loss peak (ln F_{max}) vs. temperature for TiO₂ films with anatase structure. E_a is the thermal activation energy of the dielectric relaxation.

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Fig. 4. Temperature dependent conductivity of TiO₂ as a plot of $\ln \sigma$ vs. temperature. $E_{\rm A}$ is the thermal activation energy of conductivity.

To clarify the origin of the observed activation energy, the impedance measurements were performed at different applied voltages. The frequency of the loss tangent peak was found to depend on the applied voltage (figure not shown). The observed behaviour suggests that the calculated energy of dielectric relaxation is due to the interface states [16,17].

For the material characterization a model of two impedances (SiO₂ and TiO₂) connected in series were used. The presence of interfacial SiO₂ layer was confirmed by Ellipsometry and IRspectroscopy measurements (see Section 3.2). The impedance consists of capacitor and resistor in parallel and has been used to calculate the resistance of the TiO₂ layer. To get the capacitance and resistance of TiO₂ layer we measured the impedance of the Si/SiO₂/TiO₂ structure at zero bias in the frequency range of 10 Hz-1 MHz. The obtained results were fitted by the Z'' versus Z' (Cole–Cole diagram) using the above mentioned model. Fig. 4 presents the temperature dependent conductivity of TiO₂ as a plot of $\ln \sigma$ vs. 1/T. The thermal activation energy of conductivity (E_A) is about 101 meV in TiO₂-anatase and about 63 meV in TiO₂-rutile films. Similar values are reported in literature [18,19]. It is known that electrical conductivity of TiO₂ is determined by oxygen vacancies thus the conductivity activation energy can be assigned to this donor level.

In the present work the effective dielectric constant was calculated from the slope of the linear fit of the reciprocal of capacitance (1/C) vs. film thickness at 10 kHz (figure not shown). The detailed description of the dielectric constant calculation is given in our previous paper [13]. The dielectric constant value for the TiO₂-anatase films is between 36 and 46 regardless of the annealing temperature. For comparison, TiO₂-anatase thin films prepared by spin-coating technique show dielectric constant value of 22.5 [13]. For the TiO₂ films with rutile structure the dielectric constant values of 53 to 70 were calculated.

4. Conclusions

In this work we demonstrated by Raman, FTIR and XRD studies that the structure of the spray pyrolysis deposited TiO_2 films can be easily modified by the post-deposition annealing temperatures. Nevertheless, to form the TiO_2 films with desirable crystal structure one has to choose the accurate growth temperature. The general trend is that the film roughness increases by the annealing temperature and the number of spray pulses. It is shown that the spray pyrolysis method can be applied to prepare TiO_2 films with an effective dielectric constant value of 36 to 46 for anatase and 53 to 70 for rutile at 10 kHz. The conductivity activation energy for TiO_2 films with anatase and rutile structure is found to be 101 and 63 meV, respectively.

Acknowledgement

The study is supported by the Federal Ministry of Education and Research (BMBF) under the WTZ project EST 02/001 and by the Estonian Science Foundation Grant No. 5612. For the opportunity to conduct Raman experiments, we thank Prof. Albert Goossens from the Delft University of Technology.

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