*Solid State Phenomena Vols. 99-100 (2004) pp 259-264*
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*doi:10.4028/www.scientific.net/SSP.99-100.259*

# Properties of $TiO_2$ Films Prepared by the Spray Pyrolysis Method

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**Keywords:** $TiO_2$, spray pyrolysis, structure, electrical properties

**Abstract.** $TiO_2$ thin films were prepared by spray pyrolysis method. The solution containing titanium(IV)isopropoxide, acetylacetone and ethanol was deposited onto n-type Si(100) and HD Si(100) wafers at substrate temperatures of 315 to 500 $^0$C by pulsed spray solution feed. The films were characterized by FTIR, XRD, AFM, ellipsometry, impedance and I-V measurements. As-deposited films prepared below 500 $^0$C were amorphous, whereas crystalline films could be achieved at 500 $^0$C. Subsequent annealing at 700 °C in air led to crystalline anatase formation for films deposited below 400 °C. Rutile phase appears in annealed films prepared at a growth temperature above 400 °C. Anatase $TiO_2$ films show refractive index in the range 2.20 to 2.40 and exhibit a relative dielectric constant value of 75 in the range 1 to 100 kHz. Electric breakdown occurs for 120 nm thick film at 250 kV/cm.

## Introduction

Thin film processing routes based on sol-gel dip-coating, spray pyrolysis and spin-coating are attractive because they are versatile and cost-effective. Among very interesting thin film materials processed in this way are $TiO_2$ films which have been deposited by spray pyrolysis for different applications, including gas sensor devices [1], electrodes in solar cells [2] and photocatalysts [3]. The formation and composition of $TiO_2$ films using Ti-alkoxide as precursors have been studied extensively [1, 4, 5, 6]. Much less attention has been, however, paid to the electrical properties of $TiO_2$ films deposited by spray pyrolysis technique. This paper reports on the spray-pyrolysis processing, structure, optical and electrical properties of $TiO_2$ thin films. Particular attention is paid to the effects of preparation conditions such as deposition and annealing temperatures.

## Experimental

The precursor solution containing titanium(IV)isopropoxide (TTIP) as a titanium source, acetylacetone (AcAc) as a stabilizer and ethanol as solvent was prepared using AR grade materials from Fluka. TTIP concentration of 6 vol. % and TTIP:AcAc molar ratio of 1:2 were used as starting solutions. The solution was atomized by a pneumatic spray system using compressed air as the carrier. Si (100) ($\rho$=1.0-30.0 $\Omega$cm) and HD Si (100) wafers ($\rho$=0.001-0.005 $\Omega$cm) were used as substrates. The films were deposited using a pulsed solution feed at substrate temperatures (Ts) in the range 300 to 500 °C. The pulse consisted of 1 min spray time and 1 min pause; up to 3 pulses were used. Sequential thermal treatment was made for 15 min at 500 °C followed by 30 min at 700 °C in air. XRD patterns were recorded by a Bruker AXS D5005 diffractometer. FTIR transmittance spectra of the films on Si (100) wafers in the spectrum region of 4000-400 $cm^{-1}$ on a Perkin Elmer GX-1 spectrometer. Ellipsometric investigations on a high precision DRE ELX-02C Ellipsometer equipped with a He-Ne laser source ($\lambda$= 632.8 nm) were conducted to calculate refractive index and film thickness. Surface morphology was characterized using AFM (SIS, Germany). The Electrical properties of $TiO_2$ films on HD Si (100) substrates were characterized by a computer controlled Agilent 4192A impedance analyzer. Current-voltage (I-V) measurements were performed with a Keithley 6517A electrometer. Sputtered Au electrodes with the area of $2.88 \cdot 10^{-7}$ $m^2$ were used for contacts.

**Results and discussion**

**FTIR spectroscopic study**. IR-spectra of the as-deposited $TiO_2$ films prepared at different substrate temperatures and the film annealed at 500 °C are given in Fig.1. Strong absorption in the frequency region of 400-1000 $cm^{-1}$ corresponds to Ti-O-Ti bonding and indicates the formation of a titanium oxide network [6]. As the deposition temperature is increased the absorption band with the maximum close to 440 $cm^{-1}$, characteristic for $TiO_2$ anatase state also increases. The absorptions at 1545, 1452 and 1415 $cm^{-1}$, recorded for the films prepared at temperatures of 300-435 °C, could belong to asymmetrical and symmetrical vibration of M-O-C groups [6, 7] and $CH_2$ or $CH_3$ groups, respectively [5]. The absence of above-mentioned absorptions at substrate temperature of 500 °C indicates that relatively pure films could be already exist at this temperature (Fig.1). Annealing at 500 °C leads to significant sharpening of absorption bands in the region of 600-400 $cm^{-1}$ and clearly indicates the formation of anatase phase, independent of substrate temperature.

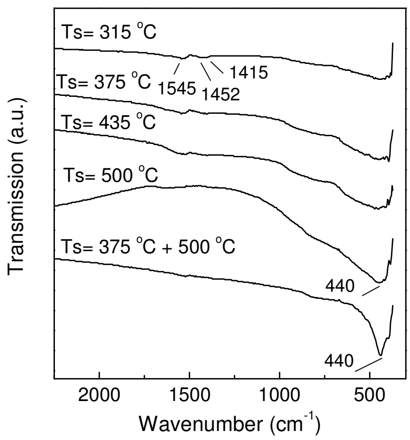


Fig.1. FTIR spectra of as-deposited films and annealed film at 500°C.

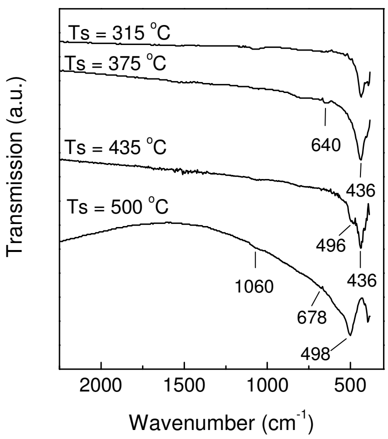


Fig. 2. FTIR spectra of the films annealed in static air at 700 °C for 30 min.

Annealing at 700 °C results in two important features according to the IR-spectra (Fig.2). The absorption peak close to 1060 $cm^{-1}$ appears, related to the stretching mode of a Si-O bond [1] and suggests $SiO_2$ formation at the interface. At the same time the formation of the well resolved peak at 436 $cm^{-1}$ can be identified for films deposited below 400 °C. The absorptions at 436 and 640 $cm^{-1}$ belong to the Ti-O-Ti vibration of the anatase phase [1]. The IR-spectrum of the sample prepared at 435 °C shows the absorptions of anatase state and the additional absorption peak at 496 $cm^{-1}$ can be attributed to the rutile phase. The IR-spectrum of $TiO_2$ film deposited at 500 °C and annealed at 700 °C clearly shows the absorption peaks at 420, 498 and 678 $cm^{-1}$ characteristic for rutile [1].

**X-Ray Diffraction study.** XRD showed the as-deposited films prepared at substrate temperatures below 500 °C are amorphous. The (101) peak of anatase (PDF 21-1272) becomes apparent for the films deposited at 500 °C (Fig. 3). Annealing at 500 °C results in anatase phase regardless of the deposition temperature as the clearly detected (101) and (200) peaks of anatase in XRD patterns confirm. Further annealing at 700 °C has a strong effect on the film structure. The films deposited at 315 °C and 375 °C are composed of the anatase phase and the increase in deposition temperature promotes the appearance of peaks characteristic for rutile phase (PDF 21-1276). The (110) peak of rutile could be detected in addition to the reflections of anatase for the films deposited at 435 °C, whereas films deposited at 500°C results in a pure rutile state according to XRD. These results are in agreement with FTIR data presented above.

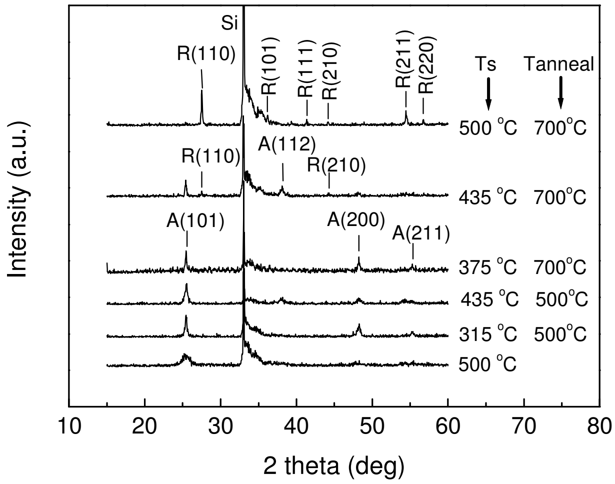


Fig. 3. XRD patterns of as-deposited and annealed $TiO_2$ films.

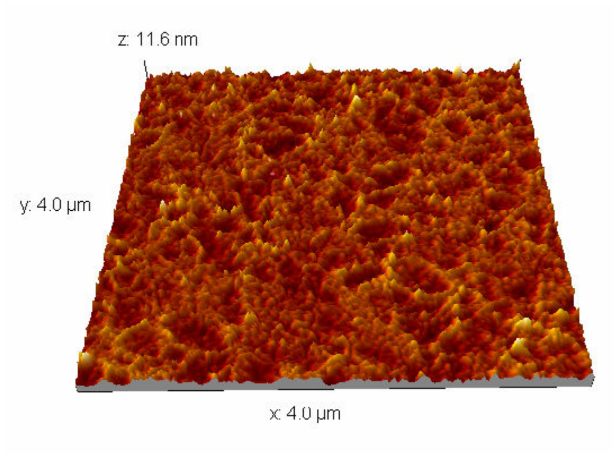


Fig. 4. AFM micrograph of the sample deposited at 375 °C and annealed at 700 °C.

**AFM study**. Fig. 4 shows an AFM micrograph of the surface morphology of the sample deposited at 375 °C and annealed at 700 °C. The film exhibits a fine grain structure and smooth surface with a calculated root-mean-square roughness of 2.6 nm. Films prepared at higher deposition temperatures show a higher roughness value.

**Ellipsometric study**. Film thickness calculated for single pulse deposited films range between 110-120 nm irrespective of growth temperatures between 300-500 °C. At the same time refractive index increased from 2.1 to 2.4 with growth temperature. The film thickness and refractive index deposited at 375 °C at spray pulses of 1 to 3 are found to be 120, 224, 266 nm and 2.2, 2.3, 2.4 respectively.

**Electrical study.** Electrical measurements were applied to annealed films with anatase structure. The capacitance dependence vs. frequency for the $TiO_2$ films of different thickness deposited at substrate temperature of 375 °C are shown in Fig.5. The frequency dispersion of the capacitance can be attributed to relaxation phenomena at the film/substrate interface and to stoichiometry gradients, and have been observed in many dielectric thin films [8]. The total capacitance $C_{TOT}$ is modelled as two capacitors connected in series, and consisting of a $TiO_2$ layer on top of a $SiO_2$ layer [9]. The dielectric constant value was calculated from the slope of fitting inverse capacitance vs. film thickness in the range of 1- 100 kHz. The effective dielectric constant was found to be 75; the capacitance of the interfacial layer was calculated to be 1 nF corresponding to an estimated $SiO_2$ thickness of 10 nm. The variation of leakage current density with electric field for a 120 nm film deposited at a substrate temperature of 375 °C is given in Fig.6. It can be seen that a steep increase in the current density is established even for a very low applied electric field, which is associated with high carrier injection across the titanium oxide film [1]. The current injection increases gradually with the applied electric field until local electric breakdown occured at an electric field of 250 kV/cm. The leakage current density is $6.8{\cdot}10^{-8}$ A/cm$^2$ at 100 kV/cm.

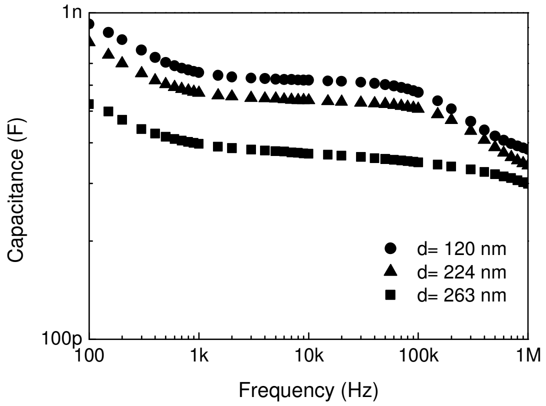


Fig.5. Capacitance vs. frequency for $TiO_2$ films deposited at 375 °C.

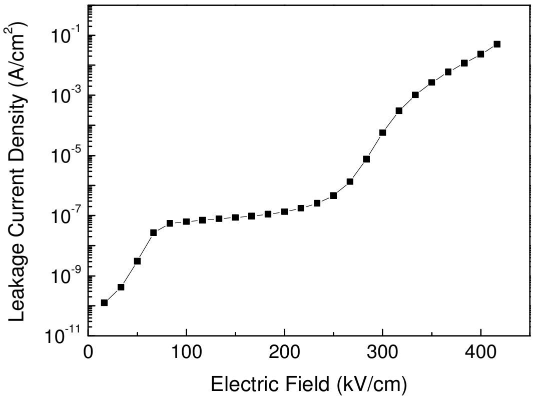


Fig.6. Leakage current density vs. electric field for 120 nm thick $TiO_2$ film deposited at 375 °C.

## Conclusions

$TiO_2$ films were prepared by spray pyrolysis at different substrate temperatures. The film thickness could be controlled by the number of spray pulses. As-deposited $TiO_2$ films grown at temperatures below 500 °C are amorphous according to XRD. The deposition or annealing at 500 °C results in anatase phase free from contaminants. Annealing at 700 °C in air leads to crystalline anatase formation for films deposited below 400 °C. Films prepared at 435 °C and at 500 °C have a mixture of anatase - rutile and rutile, respectively. $TiO_2$ anatase films grown at 375 °C and annealed at 700 °C show refractive indices of 2.2- 2.4 and a rms roughness of 2.6 nm. It is shown that cost-effective spray pyrolysis method could be used to prepare $TiO_2$ films with effective dielectric constant of 75 at 10 kHz.

## 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.

## References

[1] L. Castaneda, J.C. Alonso, A. Ortiz, E. Andrade, J.M. Saniger, J.G. Banuelos: Mat. Chem. Phys. Vol. 9486 (2002), p. 1
[2] M. Okuya, N.A. Prokudina, K. Mushika, S. Kaneko: J. Europ. Ceram. Soc. Vol. 19 (1999), p. 903
[3] M.O. Abou-Helal, W.T. Seeber: App. Surf. Sci. Vol. 195 (2002), p. 53
[4] M.J. Alam, D.C. Cameron: J. Sol-Gel Sci. Techn. Vol. 25 (2002), p. 137
[5] Y. Djaoued, R. Taj, R. Brüning, S. Badilescu, P.V., Ashrit, G. Bader, T. Vo-Van: J. Non-Cryst. Solids Vol. 297 (2002), p. 55
[6] M. Burgos, M. Langlet: Thin Solid Films Vol. 349 (1999), p. 19
[7] O. Harizanov, A. Harizanova: Sol. Energy Mat. and Solar Cells Vol 63 (2000), p. 185
[8] B. Babuji, C. Balasubramanian, M. Radhakrishnan: J. Non-Cryst. Solids Vol. 55 (1983), p. 405
[9] H. Shin, M.R. De Guire, A.H. Heuer: J. App. Phys. Vol. 10, (1998), p. 3311

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### DOI References

[2] M. Okuya, N.A. Prokudina, K. Mushika, S. Kaneko: J. Europ. Ceram. Soc. Vol. 19 (1999), p. 903
doi:10.1016/S0955-2219(98)00341-0

[3] M.O. Abou-Helal, W.T. Seeber: App. Surf. Sci. Vol. 195 (2002), p. 53
doi:10.1016/S0169-4332(02)00533-0

[7] O. Harizanov, A. Harizanova: Sol. Energy Mat. and Solar Cells Vol 63 (2000), p. 185
doi:10.1016/S0927-0248(00)00008-8

[8] B. Babuji, C. Balasubramanian, M. Radhakrishnan: J. Non-Cryst. Solids Vol. 55 (1983), p. 405
doi:10.1016/0022-3093(83)90045-5

[9] H. Shin, M.R. De Guire, A.H. Heuer: J. App. Phys. Vol. 10, (1998), p. 3311
doi:10.1016/S1359-6454(97)00258-9