Determination and Improvement of Deposition Parameters of TiO$_2$ Thin Films via ALD

Meryem Bozkaya$^1$, Ismail Kupa$^2$, Meryem Polat Gonullu$^2$, Recep Zan$^3$, Ali Kemal Okyay$^{4,5}$ and Hakan Ates$^2$

1. Department of Advanced Technologies, Graduate School of Natural and Applied Sciences, University of Gazi, Ankara, Turkey
2. Department of Metallurgical and Materials Engineering, Faculty of Technology, University of Gazi, Ankara, Turkey
3. Department of Physics, Faculty of Arts and Sciences, University of Niğde Ömer Halisdemir, Niğde, Turkey
4. Okyay Technology and R & D, Ankara, Turkey
5. Dept. of Electrical Engineering, Stanford University, CA 94305, USA

Abstract: In recent years, with the development of technology, interest in microelectronics and thin film devices has increased considerably. Future improvements in microelectronics and thin film devices are dependent on the progress of novel materials and new deposition processes. In particular, the continuing drive to some devices such as silicon devices will soon require SiO$_2$ gate and oxide layers with a thickness on the order of a few nanometers as 1 or 2 nm. Titanium dioxide is a candidate material in microelectronic and thin film devices, a wide band gap semiconductor that exhibits various crystal structures. Similarly, thin film techniques like ALD (atomic layer deposition) attract attention for the preparation of these candidate materials with higher film uniformity and conformity. Present study demonstrates how TiO$_2$ thin films were growth by ALD technique on silicon substrates at 100 °C, 150 °C and 200 °C temperatures. Different deposition conditions were examined to determine to increase film quality and efficient production of set up. XPS (X-ray photoelectron spectroscopy) technique was used to obtain the surface composition of the TiO$_2$ films. Film thicknesses and crystal structures of the films were investigated by ellipsometry and XRD (X-ray diffraction) methods. Electrical properties of the films were measured by using four probe techniques, as well. Obtained results were evaluated in terms of repeatability of recipes and application potential.

Key words: TiO$_2$ films, ALD, film grown, optical properties.

1. Introduction

Titanium dioxide (TiO$_2$) is a wide band gap semiconductor that exhibits various crystal structures such as the tetragonal anatase and rutile. Though TiO$_2$ is possibly best known for its photocatalytic properties, it is also an interesting material for dielectric and transparent-conductor applications. Owing to its higher dielectric constant, rutile is the structure-of-choice for dielectric applications, while the higher electron mobility of anatase makes it more attractive to transparent-conductor applications [1]. Amorphous TiO$_2$ thin films are studied increasingly for subwavelength optical structures due to their high index of refraction and transparency within a broad wavelength region [2]. TiO$_2$ tends to have n-type conducting character due to intrinsic defects that easily form in its crystal lattice [1]. There are many studies on TiO$_2$ in the fields of diluted magnetic semiconductors, photocatalyst materials, and electrode materials for electrochromic devices [3].

In the past two decades, it has been considered almost certainly to be the most studied transition metal oxide due to its many unusual physical, chemical, electronic, electrochemical and photoactive properties unexceptionally. TiO$_2$ has also attracted vast interest in chemical engineering related research such as solar energy conversion via dyesensitized and quantum-dot-sensitized solid-state solar cells, water splitting and general photocatalysis, lithium ion...
batteries and supercapacitors, chemical/gas sensing, controlled release, environmental remediation including indoor air purification, wastewater treatment, antifogging, self-cleaning, deodorization and deactivation of bacteria [4-6]. As the firstly reported semiconductor material for photoelectrochemical water splitting, TiO2 has been intensively studied by a large number of groups in the past decades [7-9]. Although poor ability to light absorption limits its application to a large extent, TiO2 is still an excellent assistant for other materials arising from its stability over a range of pH [9-12]. TiO2 protecting layer in the form of ultrathin film usually contains pinholes and cracks, which will activate an oxidative dissolution of the underlying substrate [13].

PVD (physical vapor deposition), CVD (chemical vapor deposition) and spin coating can be given as some of the fabrication ways of TiO2 films [14]. Aside from these growth techniques, ALD (atomic layer deposition) shows the advantage of conformal growth and precise film thickness control, which are very important to the fabrication of future microelectronic [15] and the other devices. ALD, which is one of the thin film growth techniques, has become advanced fabrication method for a rich variety of applications including complementary metal oxide semiconductor transistors, DRAM memory, energy conversion, photovoltaic, and display devices [16-18]. ALD is a cyclic vapor phase deposition technique, which takes the privilege of temporarily separated and self-limiting reactions of two or more precursors and reactants [19] that thereafter grow an ideally desired film with one specific atomic layer thickness at a time [20]. This technique facilitates the growth of various kinds of coatings including ultra-thin pure and composite layers with precise control of composition by appropriate design of ALD recipe and process details [21, 22]. In ALD technique, the precursors are pulsed to the reactor chamber one after another with intermediate purging, which results in self-limited surface reactions. A sequence consisting of one pulse of each precursor and intermediate purging is called an ALD cycle shown Fig. 1. Ideally one ALD cycle deposits a monolayer of the target compound, and thus the film thickness is accurately controlled by the total number of cycles. Doping is realized by replacing single ALD cycles of a mother compound by an ALD cycle of a dopant compound [20]. Similarly, ALD is a convenient technique for the production of good quality thin TiO2 films [23]. Obtained TiO2 thin films by using ALD techniques have been widely used in energy and environmental science due to its high chemical stability, nontoxicity and favorable energy band structure [24]. As it is known, the properties of nanomaterials depend on their shapes, sizes, crystal structures, defects, impurities, and surface areas, the potential application areas of the films will be intensely affected by these features [25, 26].

In the present study, TiO2 thin films were prepared by ALD technique on silicon substrates at 100 °C, 150 °C and 200 °C temperatures in order to determine appropriate recipe. Deposition conditions were tried to determine for increasing film quality and efficient production of set up. XPS (X-ray photoelectron spectroscopy) technique was used to obtain the surface composition of the films. Ellipsometric measurements and XRD (X-ray diffraction) analysis were carried out to determine of thicknesses and crystal structures of the films. Electrical properties of the films were measured, as well. Obtained results were evaluated in terms of repeatability of recipes and application potential.
2. Materials and Method

Depositions of the thin films included in this work were carried out in OKYAY Tech. R&D (Fig. 2) ALD reactor at various temperatures. Prior to the deposition, Si (100) which is used as substrate for production of TiO$_2$ thin film was cleaned via using standard Radio Corporation of America (RCA) cleaning methods. The pulse and purge period of ALD cycles were optimized for TiO$_2$ for three different recipes until the self-limiting and uniform growth was observed on Si (100) substrates. For the proper recipe, the precursor dose and purge times were adjusted as 0.15 and 10.0 s, respectively. For some samples grown at 200 °C, optimized recipe was used, where the dose and purge sequence for precursors was (0.015-30-0.015-30) s. The temperature range for film growth was from 100 to 200 °C. The number of growth cycles was varied from 400 to 1,200 and corresponding film thicknesses of approximately 50 to 150 nm. Various heat treatments have been implemented for characterizing of anatase and rutile phases of TiO$_2$.

XPS measurements were performed with a Thermoat a vacuum of 3×10$^{-9}$ Torr (K-Alpha-Monochromated high-performance XPS spectrometer) instrument. Deposited thin films thicknesses were characterized via spectroscopic ellipsometry measurements. Structural properties of the films were acquired by using X-ray diffraction (Bruker D8 Advance & DIFFRAC Measurement Center Software) method. The electrical characteristics, mainly the resistivity, of the materials were obtained with a four-probe resistivity measurement method by using Keithley 2400 source meter. Surface morphology was examined by using SEM (scanning electron microscopy) (an FEI Nova Nano SEM 430 microscope operated at 10 kV).
3. Results

The TiO\textsubscript{2} films were characterized by XPS technique to obtain the surface composition. The data analysis given in Fig. 3 involved spectra normalization, Shirley background subtraction, and curve-fitting Gaussian–Lorentzian line shapes [27]. Best fits were evaluated using a root-mean-square measure where line shape, peak width (FWHM) and binding energy were adjustable parameters. Shirley backgrounds were used in all fits to narrow scan spectra [28].

All XPS spectral peaks given in Fig. 3 were fitted with Thermo Scientific Avantage software. All spectra showed O 1s and C 1s spectral lines consist of a single peak (a singlet) whereas the Ti 2p spectrum consist of two peaks, a spin-orbit doublet. The C 1s spectral line was seen at 285.0 eV and the O 1s and Ti 2p spectra were adjusted to this energy. The O 1s spectrum of TiO\textsubscript{2} film has been twinned, one is peaked at 530.2 eV, and the other is peaked at 531.84 eV. The O1s spectrum of the obtained TiO\textsubscript{2} film can be determined into three peaks, one is peaked at 530.2 eV, and the other two are peaked at 531.84 eV and 532.4 eV, after annealing at 550 °C respectively. According to the literature, the main peak at the 530.2 is due to the oxygen lattice and Ti-O bond while the peaks at 531.2 eV correspond to water (O-H) and hydroxide absorbed on the surface and the peak at the 532.9 eV is probably due to the water and hydroxide Ti or basic OH on the surface [29-35].

Related to ellipsometric measurements, thicknesses of titanium dioxide films annealed at various temperatures showed the proper values ±5 nm with growth cycles. According to these results, the thin films thickness increases parallel to increasing cycles.
To clarify the crystal structure of ALD grown TiO$_2$ films, the XRD spectra was investigated which gives anatase and rutile phases after the heat treatment of 275 °C in Fig. 4. According to XRD data, the films grown at 275 °C were amorphous. All the films annealed at higher temperatures contained crystalline phases of TiO$_2$. X-ray diffraction studies revealed formation of anatase phases at $2\theta = 25.48; 37.92; 38.12; 48.20; 55.28$ and rutile phases at $2\theta = 36.04; 54.00; 62.92; 64.76; 69.12$, respectively. Also, the
Determination and Improvement of Deposition Parameters of TiO₂ Thin Films via ALD

Contents of the anatase and rutile structures and electrical properties of ALD-grown TiO₂ films annealed at various temperatures have been given in Table 1.

Table 1 also shows the calculated carrier mobility, threshold voltage, subthreshold slopes, and I_on/I_off ratios of fabricated TiO₂ devices. Extrapolation method in the saturation region (ESR) is used to extract \( \sqrt{I_D - V_G} \) characteristics of the devices [36-38]. Subthreshold slopes are extracted from \( \log (I_D - V_G) \) characteristics with \( dV_G/d\log(I_D) \) relation. Carrier mobility values were extracted from output \( I_D - V_D \) characteristics. Oxide capacitance is calculated using \( C_{ox} = \varepsilon_{ox}/t_{ox} \) and \( C_{ox} = \varepsilon_0 \varepsilon_r/t_{ox} \) relations, where \( \varepsilon_r \) denotes dielectric permittivity of ALD deposited TiO₂.

It is known that electrical properties of TFT devices follow a similar trend with outcome of XPS measurements. O/Ti ratio in the film decreases with increasing deposition temperature. This results in higher effective doping due to defects [39-41]. At low deposition temperatures, O-H bonds passivate the defects and therefore reduce carrier concentration and increase I_on/I_off ratio. Typical \( I_D-V_{DS} \) characteristics of a device annealed at 475 °C shows maximum value. A maximum I_on/I_off ratio of \( 2.5 \times 10^6 \) is recorded as 25x improved compared to the highest reported for this kind of devices up to now. After ALD growth, thin films annealed at 475 °C have the optimal Ti:O stoichiometry, therefore the lowest defect density. It can be said that this result is in good agreement with the tendency observed in threshold voltage vs. annealing temperature.

However, when the electrical properties compared with the XRD results, it is understood that the films annealed at 475 °C have the highest anatase content regarding to higher electron mobility.

SEM images of two different samples were given in Fig. 5. SEM images of the ALD grown TiO₂ films were taken at about 6 mm working distance, high vacuum mode, 10 kV accelerating voltage, X40000 for cross-sectional and X 80000 for surface image.

| T_Annealing (°C) | Anatase (%) | Rutile (%) | V_Threshold (V) | I_on/I_off | subthreshold Slope (V/dec) | Mobility (cm²/V·s) |
|------------------|-------------|------------|-----------------|------------|---------------------------|-------------------|
| 275              | 73          | 27         | -1.8            | 10²        | 6.55                      | 0.330             |
| 350              | 84          | 16         | 0.2             | 10²        | 5.21                      | 0.400             |
| 475              | 99          | 1.0        | 6.5             | 2.5×10⁶    | 0.35                      | 0.670             |
| 550              | 88          | 12         | 4.3             | 4×10⁵      | 1.36                      | 0.17              |
| 625              | 96          | 4.0        | 7.1             | 10⁹        | 0.35                      | 0.27              |

Fig. 5 SEM images of the titanium dioxide films by ALD, annealed at various temperatures: (a) cross-sectional image; (b) surface image.
images of the thin film demonstrated the homogeneous phase distribution of the TiO$_2$ (Fig. 5b). Some porosity is seen on the surface morphology of these thin films, which is influenced by the growth temperatures, annealing and process parameters. After ALD growth, thin films annealed at 475 °C have the optimal Ti:O stoichiometry, therefore the lowest defect density. It can be said that this result is in good agreement with the tendency observed in threshold voltage vs. annealing temperature.

When obtained results in all experimental studies are evaluated, it can be said that ALD thin films presented at this study are ideal candidates for microelectronic devices and optical applications.

4. Conclusion

In order to improve deposition parameters of TiO$_2$ thin films via ALD have been investigated and conclusion can be drawn as follows:

As a result, we made a comprehensive study on the deposition parameters for growth TiO$_2$ films by using ALD technique. For this purpose, various recipe and annealing temperatures have been used and ideal one determined the best one. By the way, it is tried to determine the impact of deposition condition on the structural, electrical properties of the ALD grown TiO$_2$ film. An ideal recipe showed that the growth temperature is 200 °C. Our results demonstrate that deposition parameters affect the structural, surface and electrical properties of the ALD TiO$_2$ films, as well.

Acknowledgments

Authors would like to thank Gazi University Scientific Research Unit (GUBAP), University of Niğde Ömer Halisdemir and Okyay Energy Res-Dev Engineering.

References

[1] Niemelä, J. P., Marin, G., and Karppinen, V. 2017. “Titanium Dioxide Thin Films by Atomic Layer Deposition.” Semiconductor Sciences and Technology 32 (9).

[2] Saleem, M. R., Silfsten, P., Honkanen, S., and Turunen, J. 2012. “Thermal Properties of TiO$_2$ Films Grown by Atomic Layer Deposition.” Thin Solid Films 520: 5442-6.

[3] Chen, X., and Mao, S. S. 2007. “Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Application.” Chemical Reviews 107: 2891-959.

[4] Bahnmenn, D. W., Hilgendorff, M., and Memming, R. 1997. “Charge Carrier Dynamics at TiO$_2$ Particles: Reactivity of Free and Trapped Holes.” Journal of Physical Chemistry B 101: 4265-75.

[5] Furube, A., Du, L. C., Hara, K., Katoh, R., and Tachiya, M. 2007. “Ultrafast Plasmon-Induced Electron Transfer from Gold Nanodots into TiO$_2$ Nanoparticles.” J. Am. Chem. Soc. 129: 14852-3. https://pubs.acs.org/doi/pdf/10.1021/ja076134v.

[6] He, Y. B., Tiloca, A., Dulub, O., Selloni, A., and Diebold, U. 2009. “Local Ordering and Electronic Signatures of Submonolayer Water on Anatase TiO$_2$ (101).” Nature Materials 8: 589-95.

[7] Fujima, A., and Honda, K. 1972. “Photochemical Photolysis of Water at a Semiconductor Electrode.” Nature 238: 37-8.

[8] Chen, X., Liu, L., Yu, P. P., and Mao, S. S. 2011. “Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals.” Science 331: 746-50.

[9] Luo, C., Ren, X., Dai, Z., Zhang, Y., Qi, X., and Pan, C. 2017. “Present Perspectives of Advanced Characterization Techniques in TiO$_2$-Based Photocatalysts.” ACS Applied Materials and Interfaces 9 23265-86.

[10] Kafizas, A., Ma, Y., Pastor, E., Pendlebury R. S., Mesa, C., Francès, L., et al. 2017. “Water Oxidation Kinetics of Accumulated Holes on the Surface of a TiO$_2$-photoanode: A Rate Law Analysis.” ACS Catalysis 7: 4896-903.

[11] Son, H. J., Prasittichai, C., Mondoch, E. J., Luo, L., Wu, J., Kim, W. D., et al. 2013. “Day Stabilization and Enhanced Photoelectrode Wettability in Water-Based Dye-Sensitized Solar Cells through Post-Assembly Atomic Layer Deposition of TiO$_2$.” Journal of American Chemical Society 31: 11529-32.

[12] Chen, W. Y., Prange, D. J., Dühnen, S., Park, Y., Gunji, M., Chidsey E. D. C., and McIntyre, C. P. 2011. “Atomic Layer-Deposited Tunnel Oxide Stabilizes Silicon Photoanode for Water oxidation.” Nature Materials 10: 539-44.

[13] Liu, M., Xue, F., Wang, X., Fu, W., Wang, Y., Lu, Y., and Li, N. 2017. “Conformal Deposition of Atomic TiO$_2$ Layer on Chalcogenide Nanorod with Excellent Activity and Durability towards Solar H$_2$ Generation.” Chemical Engineering Journal 341: 335-43.

[14] Zhao, C., Hedhili, M. N., Li, J., Wang, Q., Yang, Y.,
Chen, L., and Li, L. 2013. “Growth and Characterization of Titanium Oxide by Plasma Enhanced Atomic Layer Deposition.” Thin Solid Films 542: 38-44.

[15] Kim, H., Lee, R. B. H., and Maeng W.-J. 2009. “Applications of Atomic Layer Deposition to Nanofabrication and Emerging Nanodevices.” Thin Solid Films 517: 2563-80.

[16] Kim, H. 2011. “Characteristic and Applications of Plasma Enhanced-Atomic Layer Deposition.” Thin Solid Films 519: 6639-44.

[17] Sammelselg, V., Rammula, R., Aarik, J., Kkas, A., Koosser, K., and Käämbr, T. 2007. “XPS and AFM Investigation of Hafnium Dioxide Thin Films Prepared by Atomic Layer Deposition on Silicon.” Journal of Electron Spectroscopy and Related Phenomena 156-158: 150-4.

[18] Johnson, W. R., Hultqvist, A., and Bent, F. S. 2014. “A Brief Review of Atomic Layer Deposition: From Fundamentals to Applications.” Materials Today 17: 236-46.

[19] Zhuiykov, S., Kawaguchi, T., Hai, Z., Akbari, K. M., and Heynderickx, M. P. 2017. “Interfacial Engineering of Two-Dimensional Nano-structured Materials by Atomic Layer Deposition.” Applied Surface Science 392: 231-43.

[20] Leskelä, M., and Ritala, M. 2002. “Atomic Layer Deposition (ALD): From Precursors to Thin Film Structures.” Thin Solid Films 409: 138-46.

[21] Coy, T., Yate, L., Kabacifiska, Z., Tancelewicz, M., Jurga, S., and Latsunskyi, I. 2016. “Topographic Reconstruction and Mechanical Analysis of Atomic Layer Deposited \( \text{Al}_2\text{O}_3/\text{TiO}_2 \) Nanolaminates by Nanoindentation.” Materials and Design 111: 584-91.

[22] Luka, G., Wachnicki, L., Witkowski S. B., Jakiela, R., and Virt, S. I. 2017. “Structure-Property Relationships in \( \text{ZnO} / \text{Al} \)-hydroquinone Films Grown on Flexible Substrates by Atomic and Molecular Deposition.” Materials and Design 119: 297-302.

[23] Suisalu, A., Aarik, J., Mändar, H., and Sildos, I. 1998. “Spectroscopic Study of Nanocrystalline Thin Films Grown by Atomic Layer Deposition.” Thin Solid Films 336: 295-8.

[24] Edy, R., Zhao, Y., Huang, S. G., Shi, J. J., Zhang, J., Sollovev, A. A., and Mei, Y. 2016. “\( \text{TiO}_2 \) Nanosheets Synthesized by Atomic Layer Deposition for Photocatalysis.” Progress in Natural Science: Materials International 26: 493-7.

[25] Chen, K., Jiang, Z., Qin, J., Jiang, Y., Li, R., Tang, H., and Yang, X. 2014. “Synthesis and Improved Photocatalytic Activity of Ultrathin \( \text{TiO}_2 \)-Nanosheets with Nearly 100% Exposed (001) Facets.” Ceramics International 40: 16817-23.

[26] Xie, Y., Wu, Q., Liu, M., and Piao, L. 2014. “Effect of Different Base Structures on the Performance of the Hierarchical \( \text{TiO}_2 \)-Photocatalysts.” Catalysis Today 225: 74-9.

[27] Zakaznaya-Herzog, V. P., Nesbitt, H. W., Bancroft, G. M., and Tse, J. S. 2006. “High Resolution Core and Valence Band XPS Spectra of Non-conductor Pyroxenes.” Surf. Sci. 600: 3175-86.

[28] Shirley, D. A. 1972. “High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold.” Phys. Rev. B 5: 4709.

[29] Chastain, J. 1992. Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer.

[30] Young, V., and Otgawa, T. 1982. “XPS Studies on Strontium Compounds.” Appl. Surf. Sci. 20: 228-48.

[31] Briggs, D., and Seah, M. 1983. *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, edited by D. Briggs, and M. P. Seah, John Wiley & Sons, Chichester, xiv+ 533.

[32] Wagner, C., Zatko, D., and Raymond, R. 1980. “Use of the Oxygen KLL Auger Lines in Identification of Surface Chemical States by Electron Spectroscopy for Chemical Analysis.” Anal. Chem. 52 (9): 1445-51.

[33] Xiao, S. J., Textor, M., Spencer, N. D., and Sigrist, H. 1998. “Covalent Attachment of Cell-Adhesive, (Arg-Gly-Asp)-Containing Peptides to Titanium Surfaces.” Langmuir 14 (19): 5507-16.

[34] Viornery, C., Chevolot, Y., Leonard, D., Aронsson, B. O., Pechy, P., Mathieu, H. J., Descouts, P., and Gratzel, M. 2002. “Surface Modification of Titanium with Phosphonic Acid to Improve Bone Nonding: Characterization by XPS and ToF-SIMS.” Langmuir 18 (7): 2582-9.

[35] Smith, N. A., Antoun, G. G., Ellis, A. B., and Crone, W. C. 2004. “Improved Adhesion between a NiTiSMA Wire and a Polymer Matrix via Silane Coupling Agents.” Composites A—Appl. Sci. Manuf 35 (11): 1307-12.

[36] Kim, Y., Koo, J., Han, J., Choi, S., Jeon H., and Park, C. 2002. “Low-Temperature Growth of \( \text{SiO}_2 \) Films by Plasma-Enhanced Atomic Layer Deposition.” J. Appl. Phys. 92: 5443.

[37] El-Atab, N. F., Ozcan, A., Alkis, S., Okyay, A. K., and Nayfeh, A. 2014. “Low Power Zinc-Oxide Based Charge Trapping Memory with Embedded Silicon Nanoparticles via Poole-Frenkel Hole Emission.” Applied Physics Letters 104 (1): 013112.

[38] Krajewski, T., Guziewicz, E., Godlewski, M., Wachnicki, L., Kowalik, I. A., Wojcik-Glodowska, A., Lukasiewicz, M., Kopalko, K., Osinniy, V., and Guziewicz, M. 2009. “XPS and AFM Investigation of Hafnium Dioxide Thin Films Prepared by Atomic Layer Deposition on Silicon.” Journal of Electron Spectroscopy and Related Phenomena 156-158: 150-4.
[39] Pearton, S. J., Norton, D. P., Ip, K., Heo, Y. W., and Steiner, T. 2003. “Recent Progress in Processing and Properties of ZnO.” *Superlattices and Microstructures* 34 (1–2): 3-32.

[40] Ozgur, U., Alivov, Y. I., Lui, C., Teke, A., Reshchikov, M. A., Doğan, S., et al. 2005. “A Comprehensive Review of ZnO Materials and Devices.” *Journal of Applied Physics* 98 (4): 041301-3.

[41] Klingshirn, C. 2007. “ZnO: From Basics towards Applications.” *Physica Status Solidi (B)* 244 (9): 3019.