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Optical properties and morphology of PECVD deposited titanium dioxide films

J. Kowalski*, A. Sobczyk-Guzenda, H. Szymanowski, M. Gazicki-Lipman
Institute of Materials Science and Engineering, Technical University of Lodz,
ul. Stefanowskiego 1, 90-924 Łódź, Poland
* Corresponding author: E-mail address: jm.kowalski@wp.pl

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Materials

ABSTRACT

Purpose: The purpose of the present work is to compare the structure and optical properties, with respect to their potential optical applications, of titanium dioxide films synthesized with the PECVD method from two different precursor materials, namely titanium tetrachloride and titanium tetraethoxide (TEOT).
Design/methodology/approach: Optical properties as well as thickness of the films were analyzed by means of Variable Angle Spectroscopic Ellipsometry (VASE). Morphology studies were carried out by Scanning Electron Microscopy (SEM) and chemical composition characterisation was performed with the help of Energy Dispersive Spectroscopy (EDS) unit coupled with the electron microscope.
Findings: Optical parameters approaching those of titanium dioxide were achieved for both precursors. Studies of morphology show that the films produced from TEOT have favourable, smooth surface in contradiction to broccoli-like structure obtained for the chloride precursor. The type of substance used for titanium oxides synthesis determined chemical composition of the films resulting in their enrichment with either chlorine or carbon, depending on the precursor composition.
Practical implications: The optical quality of the films is good enough to suggest their applications in stack multilayer interference filters. The refractive index values of these films advocate their use as high refractive index materials while their low extinction coefficients assure the devices transparency.
Originality/value: The work presents deposition rates as well as the films optical properties, chemical composition and morphology in relation to operational parameters of their synthesis. It also provides a comparison of these characteristics for two competitive precursor compounds. Finally, it presents the capability of PECVD method for the deposition of optical coatings onto polymer substrates.
Keywords: Amorphous materials; Thin & thick coatings; PECVD method; TiO_2 thin films; Optical properties

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1. Introduction

Due to a combination of such unique properties as high refractive index, high transmittance, chemical stability and photo-catalytic behaviour, titanium dioxide constitutes a very valuable material for optical applications [1-3]. A number of techniques are used to deposit thin titania films, including PVD [4], thermal CVD [5] or sol-gel [6,7]. Plasma enhanced CVD method with its low temperature character extends potential application areas of coatings on thermally sensitive substrates like polymers[8]. Usually, titanium tetrachloride is used as the precursor compound

for the PECVD synthesis of TiO_2 either for the production of stack optical filters [9] or for the investigation of the films photo-catalytic properties [10]. However, a definite disadvantage of using $TiCl_4$ is a very corrosive nature of the process by-products, affecting process equipment as well as substrates. Under these circumstances a search for substitute precursor compounds is underway. Organic titanium derivatives make obvious candidates for the job. In the present work a comparison between titanium dioxide films produced from titanium tetrachloride ($TiCl_4$) and from titanium tetraethoxide (TEOT), using silicon wafers and transparent polyethylene terephtalate (PET) foil as substrates, is undertaken.

2. Experimental

2.1. Deposition of the films

Depositions of thin titanium oxide films from chloride precursor were performed using a parallel plate RF PECVD reactor, described previously [11,12]. Since the second investigated precursor (TEOT) requires elevated temperatures, in this case depositions were carried out in another apparatus, equipped with the supply line heating system. The heating is performed in three stages and it is applied to the container with liquid precursor, to the connecting pipe and to the shower type injection system. In order to avoid condensation, each subsequent stage has higher temperature. At the same time oxygen is introduced with a separate line. The RF power is supplied using a Plasma Products, model RF5S power generator and a self-made matching circuit. The schematic view of the TEOT reactor is presented below, in Figure 1.

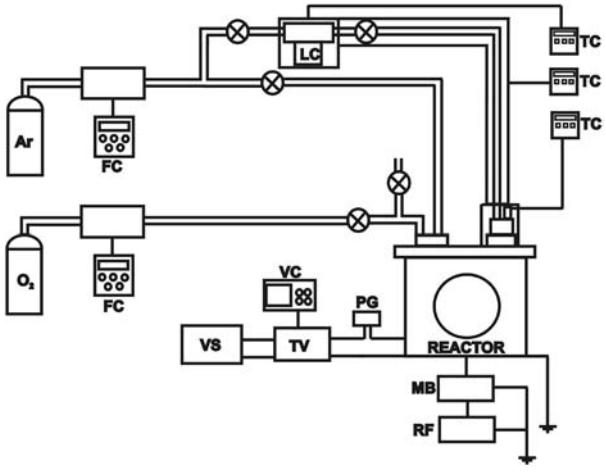

Fig. 1. A schematic representation of PECVD reactor system. System description: FC – mass flow controllers, LC – liquid precursor container compound, TC – temperature controllers, VS – vacuum system, TV – throttling valve, VC – vacuum controller, PG – pressure gauge, MB – matching circuit, RF – power generator

The flow rate of both precursors is realized by the control of the liquid container temperature. Following the initial optimization, the container temperatures were set at the level of 0^oC and 90^oC, for $TiCl_4$ and TEOT respectively. In both cases an increase of container temperature led to the deposition of non-decomposed precursor on the substrate surface followed by its condensation. Lowering of the container temperature brought about a decrease of deposition rate accompanied by worsening of the films optical parameters. In the case of films deposited onto polymer substrates lowering of the precursor temperature resulted in the fogging of these substrates. Simultaneously, other flaws began to appear on the surface. Figure 2 shows a dependence of the refractive index of titanium dioxide films on the temperature of titanium tetraoxide container, while the above mentioned defects are presented in Figure 3.

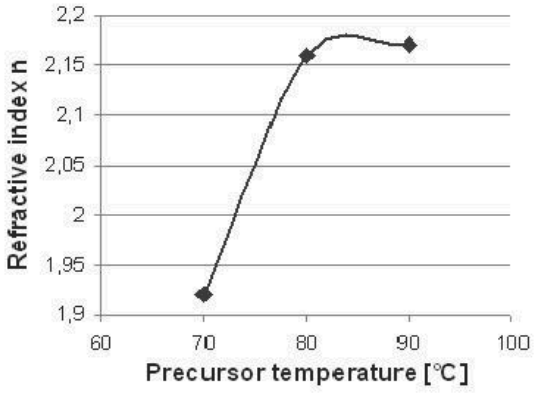

Fig. 2. The effect of TEOT temperature on refractive index of TiO_2 films

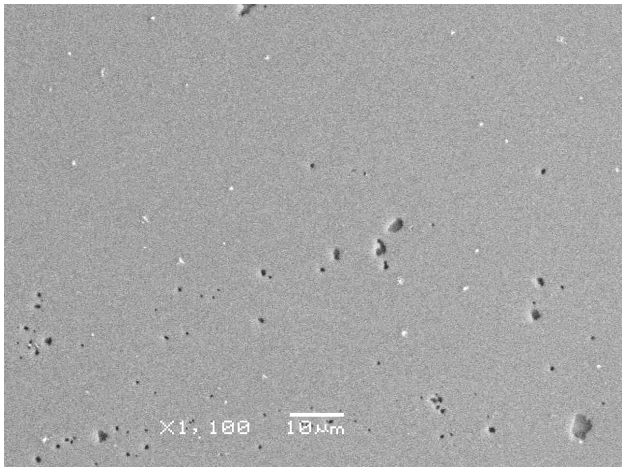

Fig. 3. SEM micrograph of defected TiO_2 film deposited on silicon wafer from TEOT of temperature equal 70^oC

2.2. Film characterisation

Optical properties, such as refractive index *n*, extinction coefficient *k*, of the titanium oxide films deposited on silicon wafers, as well as their thickness were determined by means of VASE ellipsometer manufactured by J.A. Woolam Co. Inc.

Structure of the films was investigated with the help of Hitachi F 3000 N scanning electron microscope (SEM) equipped in energy dispersive X-ray spectrometer (EDS) that was used for the determination of chemical composition of films. Observations were carried out with the acceleration voltage of 15kV and in a low vacuum mode. The pressure used in a low vacuum mode was 1 Pa for silicon wafers and 30 Pa for polymer foils.

The comparative study of both types of TiO_2 films (one resulting from $TiCl_4$ precursor and the other deposited from TEOT) concerned the effect of such operational parameters as the glow discharge power and the flow rate of oxygen. This study was preceded by an initial optimization of precursors temperature, referred to in section 2.1.

3. Results

3.1. Optical properties and thickness of the films

One of the two operational parameters which were used to optimize optical properties of the resulting titanium dioxide films was the discharge power. An analysis of its effect on the principal optical property of these films, such as their refractive index, in both cases shows an increasing relationship up to the power value of 300 W, for which the refractive index acquires its maximum value (see Figure 4).

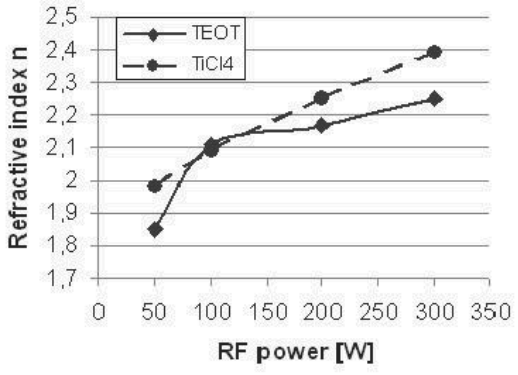

Fig. 4. The effect of RF power on refractive index

The maximum value of refractive index was slightly higher in the case of materials deposited from chloride precursor, amounting to 2.39, and to 2.25 for $TiCl_4$ and TEOT based films, respectively. Nevertheless, one can state that, in both cases, an application of the discharge power in the range between 200 and 300 W results in materials interesting enough, from the point of view of the manufacture of thin film stack interference filters, that an attempt to produce such a filter is justified. An increase of the discharge power beyond 300 W was leading to the degradation of polymer substrates. Such an effect was already observed in the course of previous work concerning a manufacture of optical filters on polymer substrates and it has been described in detail elsewhere [9].

Apart from the refractive index, the second most important optical parameter of a thin film is its extinction coefficient. The values of this parameter for the discussed films are presented in Table 1. In the case of films deposited from chloride precursor, an evident tendency is observed of decreasing extinction coefficient with increasing deposition power. For TEOT no such tendency could be noted, and all the values remain at nearly the same level. When evaluating these values from the viewpoint of potential practical applications, one can state that, with an exemption of the film deposited from chloride precursor at 50 W of discharge power, all the remaining films are characterized by extinction coefficient low enough to allow one to use them in optical applications.

Table 1.
Results of extinction coefficient measurements for different RF power settings

RF power [W]	Extinction coefficient k for λ=550nm	
	$TiCl_4$	TEOT
50	$1.63 * 10^{-4}$	$4.34 * 10^{-5}$
100	$3.82 * 10^{-5}$	$1.25 * 10^{-5}$
200	$8.51 * 10^{-6}$	$1.62 * 10^{-5}$
300	$1.99 * 10^{-6}$	$5.21 * 10^{-5}$

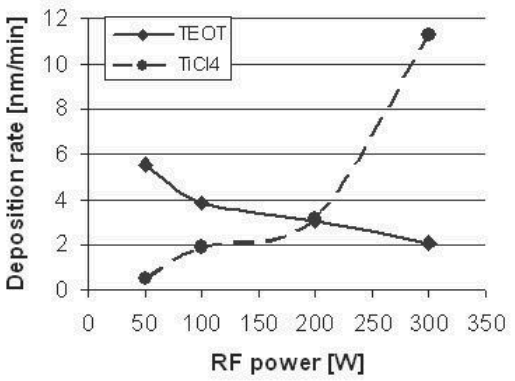

Fig. 5. The effect of RF power on deposition rate

Deposition rates of the films deposited from both precursor compounds seem to follow completely different courses. Figure 5 presents relationships of deposition rate to the discharge power for both cases. One can see that for films deposited from the chloride precursor deposition rate is an increasing function of the discharge power. This remains in contrast to the deposition rate of the organic precursor whose dependence on the discharge power is a decreasing function. The above effect appears to be resulting from the differences in the equipment used for the deposition rather than reflecting the differences in the precursor compounds.

With a detailed analysis of the deposition rate results one can note that, at the discharge power of 200W, deposition rates for both precursors are nearly the same amounting to approximately 3 nm/min. An increase of discharge power to 300W, however, brings about nearly a fivefold increase of $TiCl_4$ deposition rate and a steady decrease of that of the organic precursor.

Another operational parameter of deposition that has a definite effect on the optical properties of the films is the flow rate of oxygen. In the course of the study it turned out that the deposition of TiO_2 films from titanium tetrachloride is particularly sensitive to this parameter, giving expected effects only for a narrow range of flow rates of oxygen in the vicinity of 100 sccm. Therefore, Figure 6 presents a dependence of refractive index on oxygen flow rate for the organometallic precursor only. The results were obtained at constant discharge power of 200W. One can observe a steady increase of refractive index from the value of 2.07 for oxygen flow rate equal 150 sccm to the value of 2.21 for oxygen flow rate equal 500 sccm (Figure 6). Simultaneously, extinction coefficient was nearly the same for all the films, with the average value being $1.2 * 10^{-5}$.

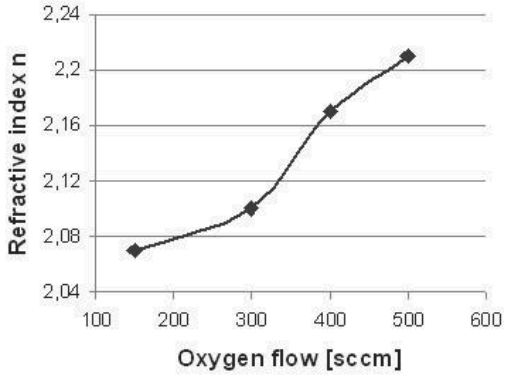

Fig. 6. Effect of oxygen flow on refractive index of films produced from TEOT

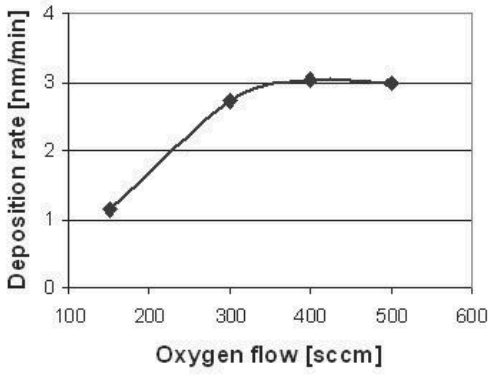

Fig. 7. Effect of oxygen flow on refractive index of films produced from TEOT

Increasing flow rate of oxygen resulted also in the acceleration of the deposition process. Initially, up to the value of 300 sccm, a clearly increasing dependence of deposition rate on the oxygen flow rate is observed. Further, for the flow rates of 400-500 sccm, this dependence saturates at the level of 3 nm/min. The entire relationship is presented in Figure 7. Both results allow one to suppose that further increase of oxygen flow rate may still be interesting from the point of view of the materials obtained.

3.2. Morphology of the films

Morphological structure of the titanium dioxide films was studied with the help of scanning electron microscopy. All the films synthesized from the organometallic precursor exhibited morphology advantageous for optical applications. These films were compact, continuos, smooth and free of defects. The only departure from that general rule concerned materials deposited under conditions of too low temperature of the liquid precursor container. These conditions, bringing about substantial deficiency of the precursor material in the discharge zone and resulting in the local discontinuities of the films, were already discussed in section 2.1. SEM image of a thin TiO_2 film deposited on silicon wafer from titanium tetraethoxide at the discharge power of 300W and the oxygen flow rate of 400 sccm is presented in Figure 8. The image is representative for the results obtained within the entire range of discharge power and oxygen flow rate conditions. What is even more important, these results appear not to be dependent on the type of substarte: similar, nearly flawless morphology was observed in the case of films deposited on polymer foil.

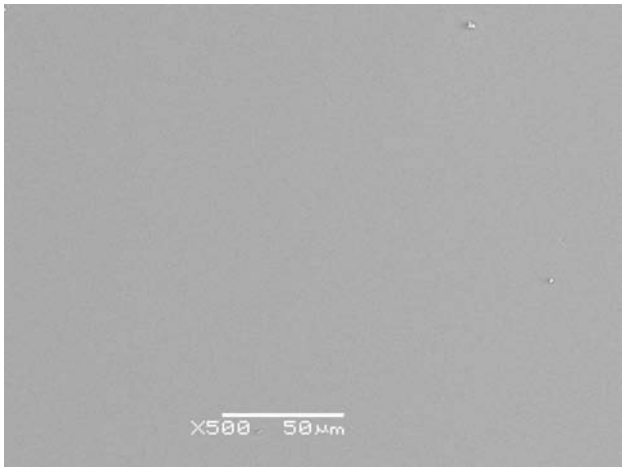

Fig. 8. SEM micrograph of TiO_2 film deposited from TEOT on silicon wafer at the RF power of 300W

As far as the films deposited from titanium tetrachloride are concerned, they have once again turned out to be strongly affected by the deposition conditions. Materials synthesized in the discharge power range of 50-100W exhibited smooth and flawless morphology, similar to that obtained in the case of titanium tetraethoxide precursor. In contrast to that, films deposited in the

Table 2.
Chemical composition of films deposited from TEOT and from $TiCl_4$ at different values of RF power

RF power [W]	Chemical composition [At.%]							
	TEOT				$TiCl_4$			
	Ti	O	C	O/Ti	Ti	O	Cl	O/Ti
100	24.2	64.7	11.1	2.67	39.2	54.5	6.3	1.39
200	26.3	65.5	8.2	2.49	34.2	62.5	3.3	1.83
300	28.9	65.6	5.5	2.27	30.5	62	7.5	2.03

power range of 200-300W, i.e. materials earlier considered the most attractive from the point of view of their optical properties, were characterized by an inhomogeneous, globular surface (see Figure 9).

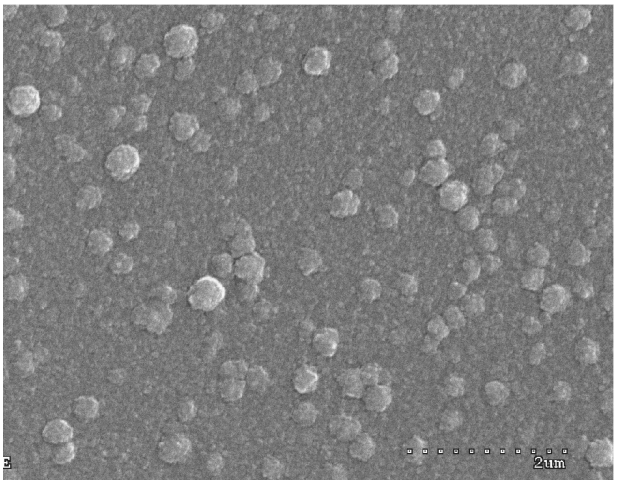

Fig. 9. SEM micrograph of TiO_2 film deposited from $TiCl_4$ on a silicon wafer with RF power of 300W

3.3. Chemical composition

Chemical composition of the films was analysed as a function of the discharge power. The results are presented in Table 2. In both cases the films have been enriched with an extra element, depending on the composition of the precursor: with chlorine in the case of tetrachloride precursor and with carbon in the case of tetraethoxide precursor. Unless it affects optical properties of the material, the presence of carbon does not pose any practical problems. A phenomenon of carbon incorporation into the films deposited from organometallic precursors is common and broadly reported [13-15]. The films obtained in the present work contain between 5,5 and 11,1 atomic % of carbon, a result which portrays itself very well when compared to the data reported by other authors. S.F. Duffant et al., for instance, present titanium oxide films deposited from TEOT, which contain up to 85 % of carbon [14]. The oxygen to titanium ratio in our films remains within the range of 2 to 3, a result very similar to that reported by N.C. da Cruz et al. for films deposited from another organic precursor, namely titanium tetraisopropoxide (TTIP) [15]. As far as the effect of increasing deposition power is concerned, it is seen in the table that the oxygen to titanium ratio decreases with that parameter, with a simultaneous decrease of carbon content. This result strongly suggests that oxygen present in the films is not exclusively bound to titanium atoms. Very probably, a fraction of oxygen atoms make connection with carbon, which explains well the oxygen to titanium ratio exceeding 2.

The films deposited from titanium tetrachloride in their composition contain chlorine at atomic content between 3,3 and 7.5 %. This is a phenomenon typical for chloride type of precursors [ref].

In this case, however, in contrast to the presence of carbon, chlorine content may have a disadvantageous influence on the potential optical or optoelectronic applications, such as interference filters, for instance, due to the possible corrosive effects. An analysis of elemental composition of the films, presented in the table, brings another important observation, this time the one concerning the oxygen to titanium ratio. A substantial increase of this ratio is observed with the increasing discharge power of the deposition. While its value amounts to only 1.39 for the films deposited at the power of 100W, it rises to 2.03 for those synthesized at 300W.

4. Conclusions

The work presents the most important, from the point of view of their potential optical applications, properties of titanium dioxide films synthesized from two different precursor compounds. Each of the two deposition process was characterized by a certain very particular specificity. Deposition from the organic titanium precursor required heating of the precursor container and the entire vapour supply system. Work with chloride precursor, on the other hand, was connected with strong corrosive effects, endangering both process stability and equipment longevity. This is the reason why two different deposition reactors were used in this work, with each process being realized in a separate apparatus. Nevertheless, the experiments were carried out in such a way that a comparison of results appears appropriate. The results obtained allow one to draw the following conclusions:

1. Films synthesized from both precursor compounds exhibit properties advantageous from the point of view of their optical applications. High values of refractive index and low extinction coefficients have been obtained for the highest levels of deposition power and, in the case of TEOT, also for the highest oxygen flow rates. An analysis of the respective relationships suggests potential for further improvement.

2. For the possible industrial applications, an optimization of deposition rates with respect to the mass production, will be inevitable.
3. The properties of films deposited from the chloride precursor are much more sensitive to the operational parameters of the deposition process than those of materials synthesized from titanium tetraethoxide.
4. Morphology of titanium tetrachloride based materials has a tendency to form non-homogeneous globular structures. This phenomenon does not take place in the case of films deposited from titanium tetraethoxide.
5. Depending on the composition of the precursor compound, films of each type contain residual amounts of an extra element. That element is chlorine in the case of tetrachloride precursor and it is carbon in the case of tetraethoxide precursor. Due to its corrosive properties, chlorine may have a disadvantageous effect on potential practical applications.

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