# Room temperature deposition of highly dense $TiO_2$ thin films by Filtered Cathodic Vacuum Arc

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## ABSTRACT

A systematic study of $TiO_2$ films deposited by dc filtered cathodic vacuum arc (FCVA) was carried out by varying the deposition parameters in a reactive oxygen atmosphere. The influence of the oxygen partial pressure on film properties is analyzed. Composition was obtained by Rutherford backscattering spectroscopy (RBS) measurements, which also allow us to obtain the density of the films. Morphology of the samples was studied by scanning electron microscopy (SEM) and their optical properties by ellipsometry. Transparent, very dense and stoichiometric $TiO_2$ films were obtained by FCVA at room temperature.

**Keywords:** Titanium dioxide, cathodic arc, optical properties

## 1. INTRODUCTION

Titanium dioxide is a wide band-gap semiconductor used in many energy-conversion and environmental applications.[1] Its outstanding physical and chemical properties include high refractive index, high chemical stability, high dielectric constant, photocatalytic activity and transparency in the visible and the near infrared. However, those properties depend to a great extent on the deposition technique employed for its fabrication. A careful control of the fabrication process is critical to optimize this material for the desired application. Several physical and chemical deposition methods have been employed to prepare $TiO_2$ films such as sol-gel, spray pyrolysis, magnetron sputtering, chemical vapor deposition, filtered cathodic vacuum arc (FCVA), etc.[1] In particular, physical vapor deposition (PVD) techniques are the preferred ones for those applications in which long-term stability and controllable optical properties play an important role, and among them magnetron sputtering (MS) is the most employed. In the present study, an alternative technique, the cathodic arc PVD, has been used to fabricate titanium dioxide thin films.

Energy of particles during deposition by cathodic arc is much larger than in others widely employed PVD techniques such as magnetron sputtering.[2] The high kinetic energy of the ions and the high ionization of the plasma during deposition can produce dense films with a good interlayer adhesion. The main drawback of this technique is the evaporation of macroparticles as a consequence of the very high ionization rate. Those macroparticles can be up to few micrometers in diameter,[3] and are specially detrimental for optical and electronic applications. In addition, they can lower the substrate/layer adhesion and lead to the formation of pin hole effects. However, the use of a curved plasma duct filter can prevent those macroparticles of reaching the substrates[4,5] and several authors claimed that filtered cathodic vacuum deposition FCVA deposition of metal oxides are preferred over other PVD techniques in terms of refractive index and extinction coefficient.[3]

$TiO_2$ films properties deposited by cathodic arc depend on many factors such as oxygen partial pressure, working pressure, arc current, presence or not of electromagnetic filter, substrate temperature, substrate bias, etc. The last two factors, temperature and bias, play an important role on the films structure due to the kinetic energy involved. The high ion energy during FCVA deposition process can favor the formation of crystalline $TiO_2$ even during deposition at room temperature. Moreover, as the plasma is highly ionized the impact energy of the ions at the surface can be controlled by applying a bias to the substrate. Several authors have reported the formation of crystalline $TiO_2$ at room temperature by applying a bias to the substrate avoiding any post or simultaneous annealing treatment. There are also reports on anatase $TiO_2$ deposition at room temperature with no applied bias.[2] For many applications this could be a great advantage, for example, when depositing on heat-sensitive substrates.[6]

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In this work, titanium dioxide films were prepared by FCVA at room temperature in a reactive oxygen atmosphere. The oxygen partial pressure (concentration percentage of the $O_2$ introduced in the total flow gas) was varied from 10 to 75% and the effect on film properties was analyzed. The composition of the obtained films was analyzed by Rutherford backscattering spectroscopy (RBS), the morphology of the samples by scanning electron microscopy (SEM) and their optical properties by ellipsometry measurements. RBS data showed that resulting films exhibit $TiO_2$ stoichiometry, with porosity below 4%. The low porosity is confirmed by SEM cross sectional images. Index of refraction does not change significantly with the oxygen ratio and values around 2.5 at 550 nm are obtained for the studied samples. We demonstrate that it is possible to obtain highly dense $TiO_2$ films with excellent properties by FCVA deposition at room temperature.

## 2. EXPERIMENTAL SECTION

TiOx films were grown on Si (100) and glass substrates by means of the dc Filtered Cathodic Vacuum Arc (FCVA) system shown in Figure 1a (PFCVA-450 from Plasma Technology Limited, Hong Kong). The system is provided by a 90º curved electromagnetic filter which guides the ions in the plasma to the deposition chamber. The substrates were placed 240 mm away from the filter duct exit. For each deposition process base pressure in the chamber was ~2 $\cdot 10^{-3}$ Pa. Prior to deposition, samples were sputter cleaned by $Ar^+$ bombardment for 15 minutes. A Ti cathode with 65 mm diameter was used for the deposition (Figure 1b) of TiOx films in an oxygen/argon atmosphere. The total working gas flow was fixed in 60 sccm, and different percentages of reactive gas during depositions were obtained by changing the $Ar/O_2$. The cathode current used was 50 A. All the depositions processes were carried out at room temperature. Deposition time was 60 minutes and the substrate holder was rotating during the whole process at 5 rpm. Depth-resolved composition of the samples was determined by Rutherford backscattering spectroscopy (RBS) using $^{4+}$He incident ions with an energy beam of 1.7 MeV. Spectra were collected with $^{4}$He ions with an energy beam of 1.7 MeV .The data were acquired with a silicon barrier detector located at a backscattering angle of 170º, with and energy detector resolution of 13 keV. The experimental spectra were fitted using the SIMNRA software. The thickness of the films was measured using a mechanical stylus profilometer (Veeco Dektak 150). Morphology was analyzed by scanning electron microscopy (SEM) with a system Hitachi S4800 SEM-FEG microscope of high resolution (1-3 nm), equipped with a Bruker X flash 4010 EDX detector with a resolution of 133 eV, field emission gun and STEM detector system. Spectroscopic Ellipsometry (SE) was used to determine the refractive index *n*, of the samples. Measurements were performed in a rotating compenstor ellipsometer M-2000FI (J.A. Woolam, Inc.).

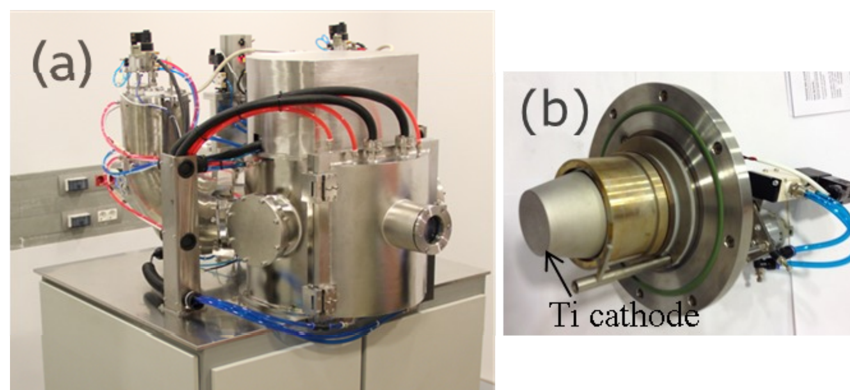


Figure 1 FCVA system (a) and arc source with Ti cathode (b) used for sample deposition.



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## 3. RESULTS AND DISCUSSION

Samples were deposited keeping the total gas flux ($O_2$+Ar) at 60 sccm and varying the relative gas flows from 10 to 75% $O_2$. Deposition time was 60 minutes and sample holder was rotating during the whole deposition process. In Table 1 a summary of the main deposition parameters for each sample can be found.

Table 1. TiOx films deposited with a constant total flux of 60 sccm, t = 60 min, with rotation

| Sample | Ar (sccm) | $O_2$ (sccm) | $O_2$/(Ar+$O_2$) (%) | Pressure (Pa) |
|---|---|---|---|---|
| S1 | 54 | 6 | 10 | 0.50 |
| S2 | 48 | 12 | 20 | 0.46 |
| S3 | 40 | 20 | 33 | 0.43 |
| S4 | 20 | 40 | 67 | 0.28 |
| S5 | 15 | 45 | 75 | 0.26 |

The working pressure for the different deposition processes is also shown in Table 1. Contrary to expectations working pressure is different for each $O_2$/Ar ratio, ranging from 0.5 to 0.26 Pa, even when the total gas flow (60 sccm) is maintained. A plausible reason for this behavior is the chamber configuration in which the oxygen enters directly into the main housing of the chamber meanwhile argon inlet is placed close to the cathode (Figure 1). In Figure 2 an image of the deposited samples can be found. Films exhibit good adhesion and they are transparent except from the sample S1, which was deposited with the lowest oxygen ratio (10%) (Table 1). Transparent samples exhibit a gradient color due to interferences, due to non-homogeneity of the thickness along the substrate (~30 nm variation). Visual inspection reveals that deposition is highly influenced by the oxygen flow at low $O_2$ ratios. By varying from 10 to 20 % the oxygen percent with no significant change in the working pressure, transparent samples are obtained. Previous works related lower transmission in TiOx films prepared with low pressures to oxygen-deficient films, which causes light absorption by free carriers from $Ti^{2+}$ and $Ti^{3+}$ species.[7] According to these authors transmittance is closely related to stoichiometry of the samples.

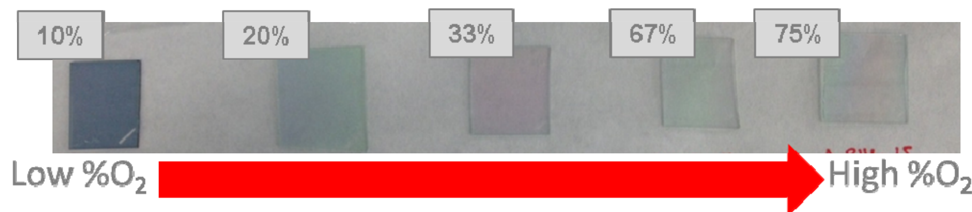


Figure 2 Pictures of samples deposited on glass

In Figure 3 deposition rates in nm/min as a function of the oxygen partial pressure are plotted. Two glass substrates and two silicon substrates were coated in each process. Their position in the sample holder can also be observed in the figure. Deposition rates increase with the oxygen flux from 2 nm/min for low oxygen flux to more than 10 nm /min for the highest oxygen flux. However, as the variation of oxygen ratio also leads to variation in the working pressure (see Table 1), this thickness trend can be also due to the lower working pressure at high oxygen ratios. According to Figure 3, deposition rate is more affected by the substrate position than by the type of substrate. Similar deposition rates are found on silicon and glass substrates. The deposition rates obtained in the present work are lower than that previously reported for $TiO_2$ films deposited by non-filtered cathodic arc and filtered cathodic arc with an applied substrate bias.[5] The lower deposition rate could be related to a lower kinetic energy of the ions. We do not observe poisoning of the cathode under reactive conditions during deposition by filtered cathodic vacuum arc.[8] This could be the reason that, in contrast to a magnetron sputtering process, no two regimes can be distinguished in the deposition rate as a function of the oxygen partial pressure.[9]



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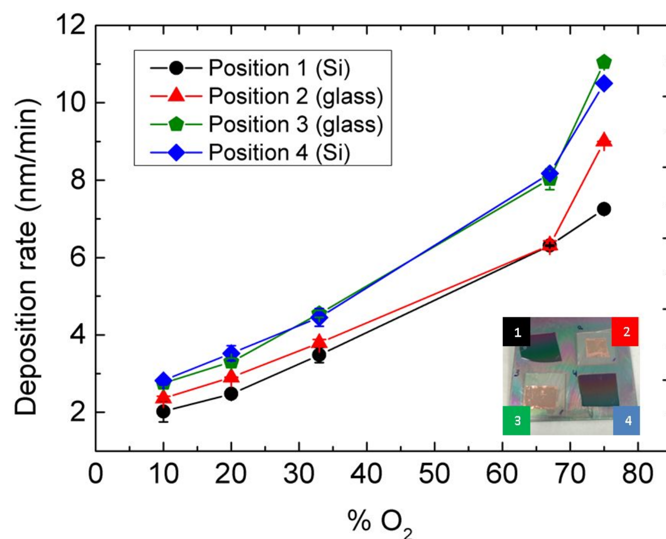


Figure 3 Deposition rate versus relative oxygen gas flux for samples deposited with a constant total flux of 60 sccm and picture of the substrates in the samples holder.

Morphology of the samples was investigated by SEM. Figure 4 shows the SEM film cross section and surface images for the sample deposited with the 33% $O_2$. Similar results were obtained for the whole range of oxygen ratios analyzed in this work. According to SEM images films exhibit a good adhesion to the substrate and they are highly dense. Dense structures and good substrate/film adhesion are very often obtained by cathodic arc deposition. The high energy of the incident particles can lead to a certain degree of implantation and also lead to suppression of columnar growth, obtaining very dense structures without the need for heating the substrate.[3] As mentioned in the introduction, one of the main drawbacks of cathodic arc deposition is the presence of macroparticles as a consequence of the high ionization currents. The surface scanning images of our samples (Figure 4) revealed a uniform and flat surface showing that the curved magnetic filter effectively avoids macroparticle deposition.



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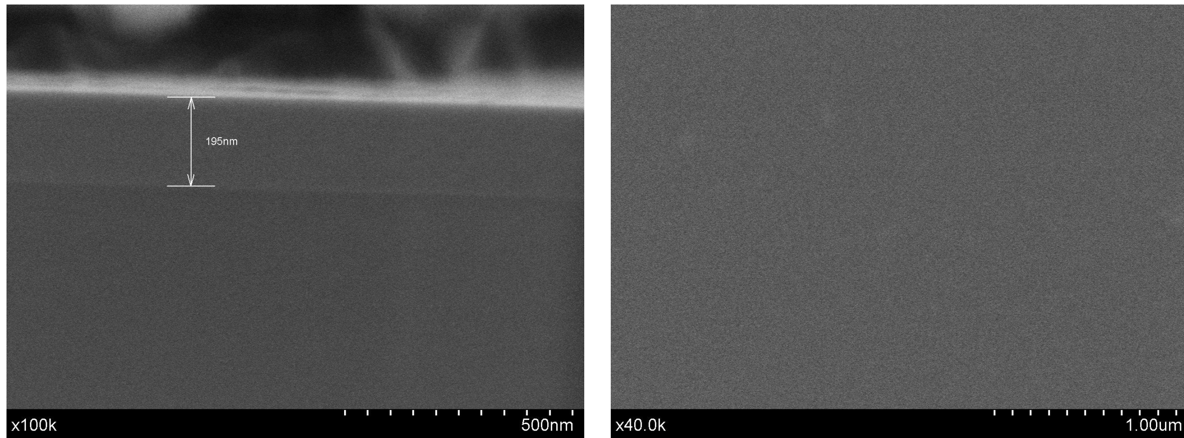


Figure 4 SEM cross section and surface images for samples S3 (33% $O_2$)

Elemental composition of films will greatly determine TiOx properties. In Figure 5 RBS measured spectrum for sample S2 (20% $O_2$) is plotted as an illustrative example. Simulation results are also included in the graph to show the accuracy of the fitting. For clarity the individual contribution of the different elements to the global spectrum has been also included in the graph. Silicon signal originated from the substrate and oxygen and titanium signals from the film can be observed. The spectra exhibits sharp edges with no tails and the data can be properly fitted using a single layer. This means that Si/$TiO_2$ interface is very narrow, down to the limit of the technique (i.e. $\pm 50 \times 10^{15}$ at/$cm^2$ or ~5 nm).[10]

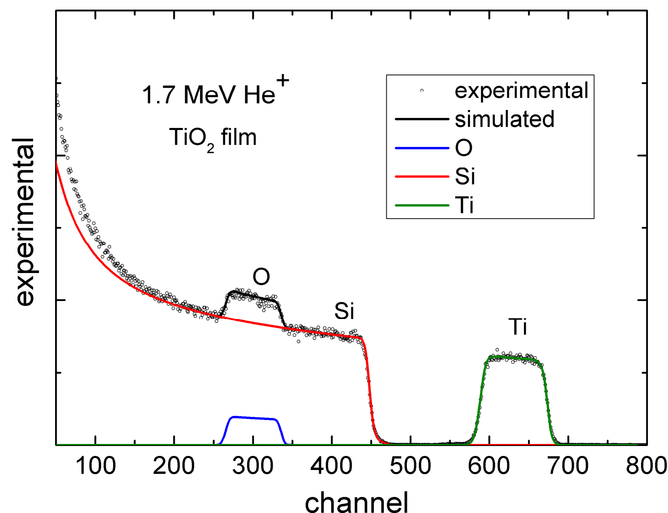


Figure 5 RBS data and simulation results for S2 sample (20% $O_2$)

Ti/O ratio for the different samples is summarized in Table 2. RBS results indicate that stoichiometric $TiO_2$ films (Ti/O 33/67) were formed and that the composition is uniform throughout the thickness of the films. Interestingly, RBS results show that stoichiometric $TiO_2$ is obtained even for the lowest oxygen percentage $TiO_2$ films (S1), and the oxygen content in the films does not vary with the $O_2$ partial pressure. This means that small variation in the stoichiometry of the samples (non-detectable by RBS) lead to opacity of the samples.[11] Sample deposited with the lowest oxygen ratio (S1) is close to sub-stoichiometry, which is further confirmed by ellipsometry measurements.



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Table 2. RBS data for TiOx films deposited with a constant total flux of 60 sccm, t = 60 min, with rotation. Film thickness measured by profilometry is also included.

| **Sample** | **$O_2/(Ar+O_2)$ (%)** | **Ti** | **O** | **Thickness ($10^{15}$ atoms/cm$^2$)** | **Thickness Profilometer (nm)** |
|---|---|---|---|---|---|
| S1 | 10 | 32±1% | 68±1% | 1635 | 169 |
| S2 | 20 | 32±1% | 68±1% | 1697 | 211 |
| S3 | 33 | 31±1% | 69±1% | 2355 | 267 |
| S3 | 67 | 32±1% | 68±1% | 3919 | 490 |
| S4 | 75 | 32±1% | 68±1% | 5582 | 630 |

RBS analysis allows calculating the corresponding areal density for each film component (atoms/cm$^2$). The same trend from the deposition rate for thin film thickness with the oxygen partial pressure shown in Figure 3 (higher deposition rate with the increment of the oxygen ratio) can be inferred from RBS data. Provided the film thickness is known from profilometry or other techniques, film density of our $TiO_2$ films can be obtained from RBS data using the relation shown in Equation 1[12]:

$$d(nm) = \frac{10^7(nmcm^{-1})t(atcm^{-2})M_n(g)}{\rho(gcm^{-3})N_A(atmol^{-1})N(mol)} \tag{1}$$

where $d$ is the film thickness, $t$ is the areal density in at cm$^{-2}$, $M_n$ is the molecular weigth, $\rho$ is the film density, $N_A$ is the Avogadro number and $N$ is the number of mols. In Figure 6 RBS thickness in at cm$^{-2}$ versus the nominal thickness in nm for the different samples is plotted. A very good linear fitting is obtained, indicating that density is similar for all the deposited samples. Therefore variation in the oxygen rate does not have a significant effect on the film density. Theoretical density value for bulk anatase and rutile materials are 3.84 gcm$^{-3}$ and 4.23 gcm$^{-3}$ respectively.[2] A density of 3.79 g cm$^{-3}$ for the deposited samples is inferred from the plot (Figure 6). This value is in agreement with Bendavid et al.[2] who reported a density of 3.80 g/cm$^3$ for $TiO_2$ films deposited by FCVA with no bias applied to the substrate. If we consider a bulk density of 3.9 g/cm$^3$ for amorphous $TiO_2$,[13,14] deposited films exhibit a porosity of 4 %, which is consistent with the dense structure observed in the SEM cross section image in Figure 4.

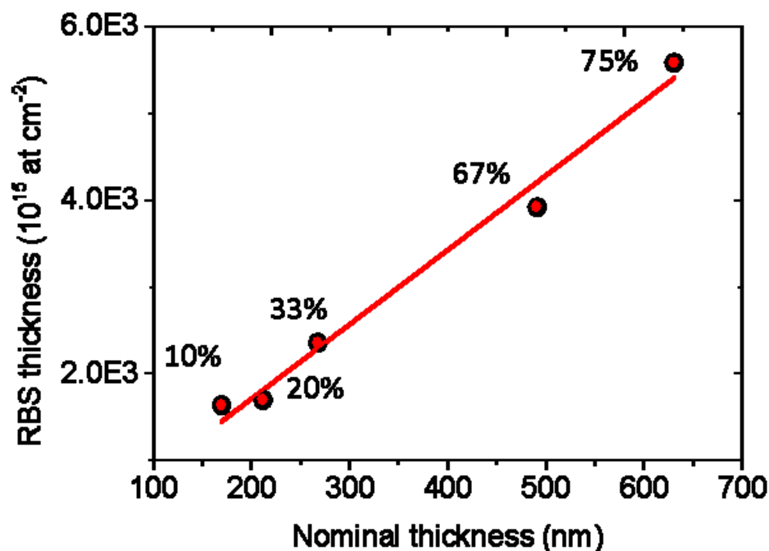


Figure 6 RBS in at cm$^{-3}$ obtained from RBS data versus nominal thickness measured by profilometry



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Refractive index was obtained from spectroscopic ellipsometry. All the samples were simulated using a Cody-Lorentz model, except from sample S1 (10% $O_2$). In this case, an additional Drude oscillator is needed to obtain a reasonable fit. This could be an indication that when depositing at low oxygen ratio we are close to the transition from $TiO_2$ to $TiO_x$ ($x<2$). Refractive indexes for the different samples are plotted in Figure 7.

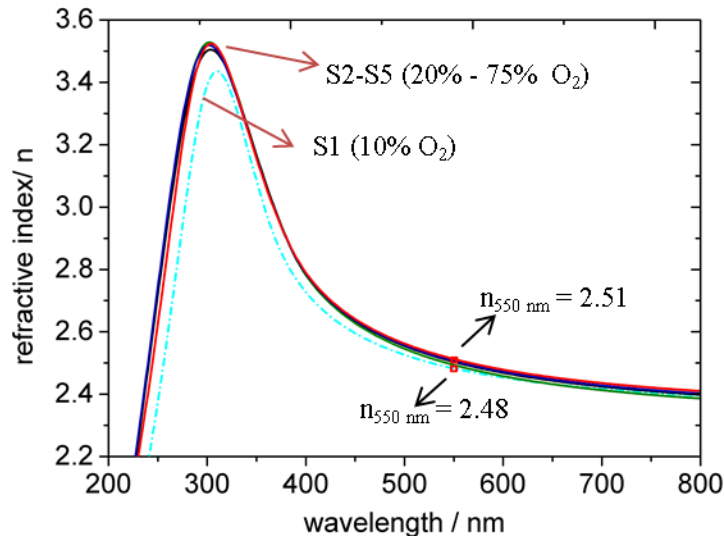


Figure 7 Index of refraction for the different deposited samples.

There are not significant differences in the refractive indexes (*n*) for the different samples except from S1. The refractive index is slightly lower for the sample with the lowest $O_2$ ratio for wavelength below 600 nm. Like all samples exhibit a similar density, the lower *n* could be related to changes in the microstructure such as the degree of cristallinity and/or phase transformations.[2] Previous work reported the following refractive indexes at 550 nm for $TiO_2$ films deposited by filtered cathodic arc: 2.56 for amorphous $TiO_2$, and 2.62 and over 2.7 for anatase and rutile phases respectively.[8] Indexes of refraction in the present work are around 2.5, being slightly lower for the sample S1 as previously mentioned. This value is therefore close to the one reported for amorphous $TiO_2$.[8] Deposition of $TiO_2$ at room temperature by physical vapour deposition usually lead to amorphous $TiO_2$, although there are some previous references of anatase phase obtained at room temperature.[5,15] Further investigations are needed to elucidate the crystalline phase of our samples.

## 4. CONCLUSIONS

Titanium oxide films were deposited by evaporating titanium ions in an oxygen environment using a filtered cathodic vacuum arc system. The effect on the film properties of oxygen ratio during deposition was analyzed. Transparent samples are obtained when the oxygen is higher than 10%. SEM images show very dense films with no presence of macroparticles on the surface. The high density is confirmed by RBS measurements which also indicate that samples exhibit a similar density, no matter the deposition conditions. Ion beam analysis shows that stoichiometric titanium oxide samples are obtained in all cases. Refractive indexes around 2.5 are obtained. Further characterization of the samples by X-Ray diffraction and Raman is needed to study thin films cristallinity. Our results indicate that high quality $TiO_2$ films, stoichiometric and with a dense structure can be obtained by filtered cathodic arc deposition at room temperature.

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