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Synthesis of TiO_x and CrO_y coatings prepared at high temperature

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Morphological and structural evolution of titanium oxide and chromium oxide films D.C. and R.F. sputtered were investigated. These materials were deposited on fused quartz and silicon wafers from pure metallic targets in mixed Ar-O_2 discharge. Transformations of the optical properties and crystallographic structures were observed for layers deposited at high temperature. The influence of D.C. or R.F. polarization on some characteristics of the coatings was also investigated. Both materials showed an amorphous structure for substrate temperatures up to 400 °C and a clear increase of layer density was illustrated from optical measurements. R.F. sputtering exhibited a strong effect on microstructure of the films compared to D.C. sputtering. This observation is discussed and some explanations of this phenomenon are proposed. *© 2000 Kluwer Academic Publishers*

1. Introduction

The deposition of thin compound films has become increasingly important for corrosion protection [1–3], wear resistance [4, 5] and the fabrication of optical and electronic devices [6–9]. Various deposition techniques such as chemical vapor deposition, ion plating, sol-gel processes and sputtering have been used for the production of metallic or compound films [10–15]. So, the growth of metallic oxide films by reactive sputtering has received a great deal of attention during the past decade due to its capability to achieve high quality films but also, because it is an industrial application to large-area deposition [16–24]. Chromium oxide and particularly titanium oxide films are extensively used in optical thin film device applications because of their desirable optical properties and good stability in adverse environments. Substrate temperature, starting material and deposition parameters can affect the durability of the films.

In this paper, we report the preparation of titanium oxide and chromium oxide layers deposited by D.C. and R.F. reactive magnetron sputtering technique. The effect of the substrate temperature in the range 20–500 °C on some optical properties and structural characteristics are investigated and compared with previous results obtained from a study concerning annealing treatment of the coatings [25]. An increase of the packing density is observed for high substrate temperature and crystallization of the layers occurs when the temperature increases. A comparative study between D.C. and R.F. polarization is also carried out for both type of materials. Oxide layers prepared from R.F. reactive sputtering exhibit higher optical properties than those D.C. deposited. These differences are discussed in order to better understand the influence of the polarization on morphological and structural properties of the coatings.

2. Experimental details

Chromium and titanium oxide thin films were prepared by D.C. and R.F. reactive magnetron sputtering in a SCM 650 (Alcatel) magnetron sputtering system which is capable of giving an ultimate vacuum of order of 10^{-5} Pa, using a turbomolecular pump-mechanical pump combination. High purity argon and oxygen were used as the sputtering and reactive gases respectively. A circular magnetron (200 mm diameter) was used as cathode and could be supplied by a 3 kW D.C. generator or a 1.2 kW R.F. generator (13.56 MHz). The experiments were performed at a constant R.F. power of 1000 W and D.C. power of 600 W, and the usual target-substrate distance was 6 cm. Pressure was monitored using Pirani and Penning gauges and the pressure of the process was measured with a capacitive Baratron gauge (MKS). The pressure of the sputtering chamber was pumped down to 5×10^{-5} Pa prior to deposition and argon was introduced in order to get a constant pressure of 0.7 Pa. Discharge was ignited to presputter the target and oxygen was injected to give a total sputtering pressure of 0.9 Pa but also, to fully poison the surface of the target [26, 27]. Oxygen flow rates used to deposit oxide materials from titanium and chromium targets were determined from previous investigations [28] so as to keep experimental conditions after instability regions currently observed in reactive sputtering [29–33]. TiO_x and CrO_y coatings were deposited on (100) silicon wafers and fused quartz substrates. The substrates were heated using an Eurotherm heater before and during deposition and the set pointed temperature was maintained within ±15 °C. The thickness of the films was determined mechanically with a Dektak 3030 profilometer. Optical properties like refractive index of the films deposited on quartz substrates were obtained by measuring the optical transmission of the transparent layers for wavelengths included between 200 to 1100 nm and by making use of a calculation method described by Swanepoel [34]. The spectral transmittance of the layers was recorded with a Perkin-Elmer UV-visible double beam spectrophotometer. X-ray diffraction analyses were obtained by a Siemens-Inel computer controlled diffractometer using Cobalt Kα radiation and the results were compared with powder diffraction file cards.

3. Results and discussion

3.1. Titanium oxide coatings

Transmittance spectra in the UV-visible region have been recorded for titanium oxide thin films prepared at different substrate temperatures from D.C. reactive sputtering; the results are shown in Fig. 1. Typical interference fringes are observed due to multiple reflections in the layer. These coatings have been prepared for the same deposition time and thickness of about 6000 Å have been measured. The effect of the substrate temperature have been studied and it can be seen that the maximum and minimum positions of the interference fringes are shifted to higher wavelengths with the substrate temperature. One can suppose that sticking probability of sputtered particles and oxygen decreases when temperature increases or, diffusion phenomena at the surface is improved. It can be also noticed that the film transmittance decreases with temperature. Narasimha Rao *et al.* [35] observed the same evolution. The decrease of transmittance of TiO_x films with substrate temperature may be mainly a result of insufficient incorporation of oxygen in the films during deposition since the condensation of oxygen decreases at elevated temperatures [36, 37]. We can also suppose that the film non-uniformity and the crystallographic changes probably affect the transmittance of the films. So, some morphological changes are likely to be the major contributions that may be responsible for the optical transmission evolutions.

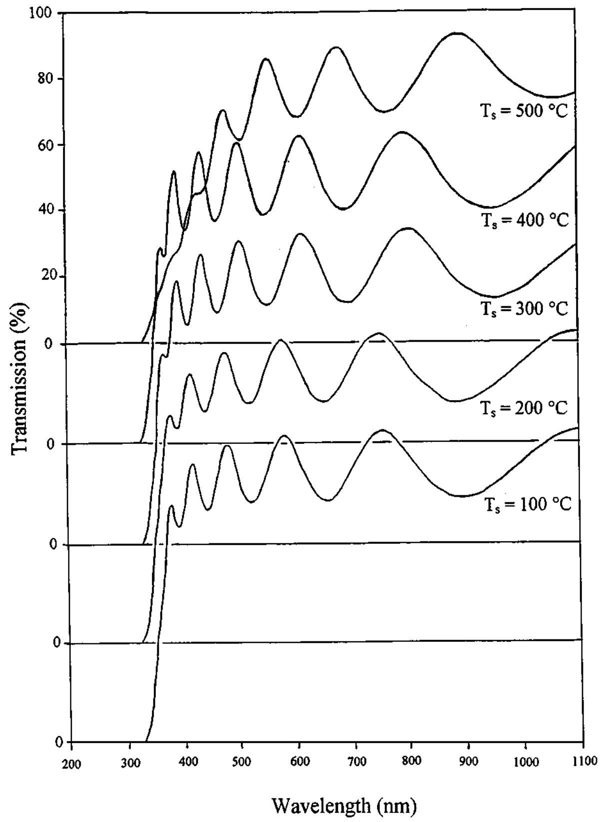

Figure 1 UV-visible transmission spectra of titanium oxide coatings D.C. deposited on fused quartz for different temperatures of the substrate. Interference fringes can be used to determine some optical properties of transparent coatings like refractive index.

In the region of the absorption edge, it is interesting to notice that TiO_x films deposited at various substrate temperatures exhibit an absorption edge that moves towards shorter wavelengths up to a temperature of 400 °C. This is a UV-shift of the absorption edge and so a reverse evolution of the gap energy is not clearly explained but this phenomenon has also been observed by other authors [38, 39]. When the substrate temperature increases again to reach 500 °C, the absorption edge is shifted to higher wavelengths. So, one can suppose that another phenomenon certainly occurs due to crystallographic evolution observed from X-ray diffraction analyses (see Fig. 3).

Refractive indexes of titanium oxide coatings D.C. sputtered have been calculated from UV-visible spectra from Fig. 1. Fig. 2 shows the evolution of this optical property versus wavelength for different substrate temperatures. It can be said that refractive index n can be expressed as a function of wavelength λ in the form of a Cauchy function such as [40]:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

where the coefficients A, B and C are constant depending on the type of material. Fits of the experimental data have been carried out to illustrate the evolution of refractive index with wavelength. The effect of the substrate temperature can be clearly observed in this figure. Refractive index always increases with the temperature. Since this optical characteristic is closely linked to the density of the layers, it can be said that a high substrate

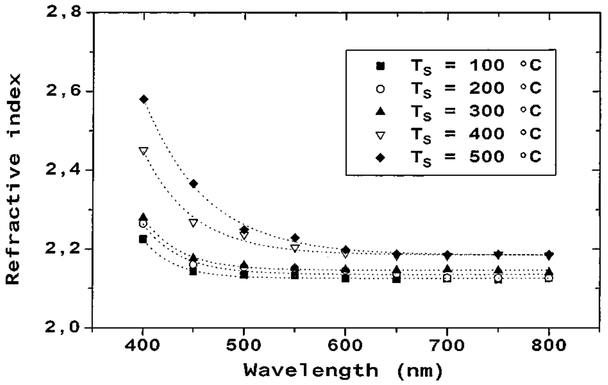

Figure 2 Evolution of refractive index n with wavelength of TiO_x thin films prepared by D.C. reactive magnetron sputtering for various substrate temperatures. High temperatures induce an increase of refractive index.

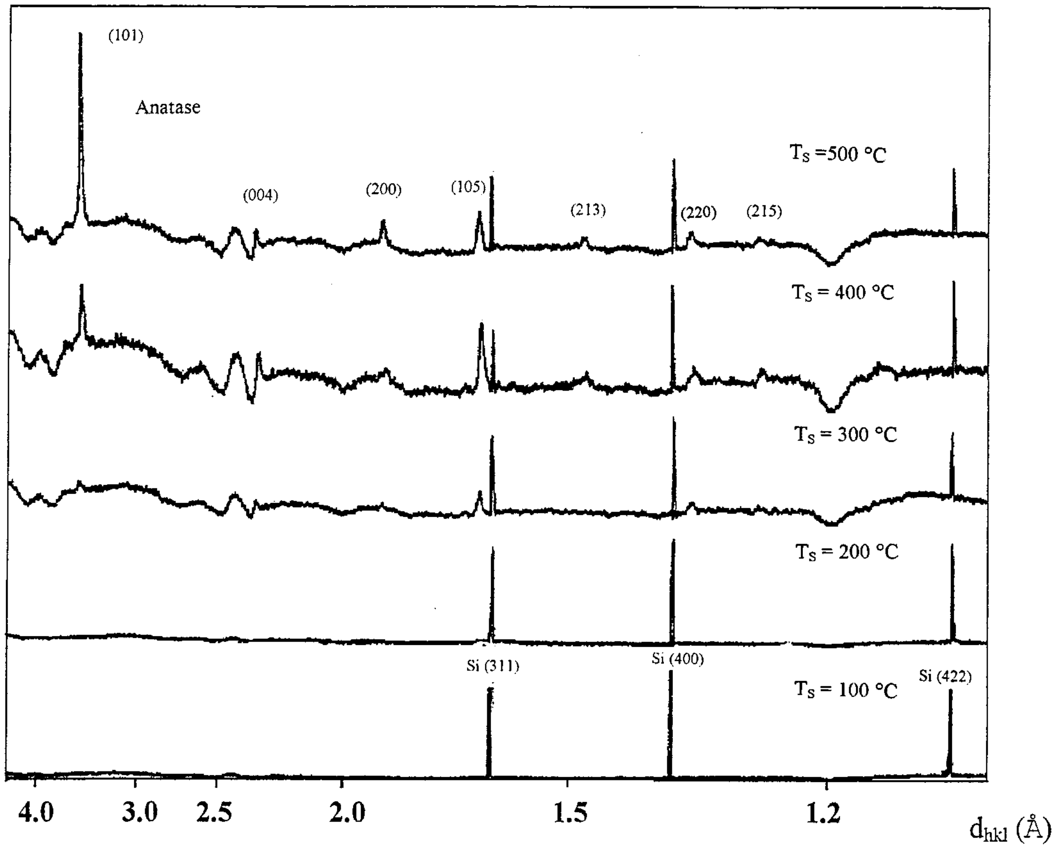

Figure 3 X-ray diffraction spectra for TiO_x coatings D.C. sputtered on (100) silicon wafers. Low substrate temperature produces amorphous materials. When temperature increases, Anatase structure is clearly observed and textured films can be obtained at 500 °C.

temperature induces a densification phenomena of the coatings. Then, the increase of refractive index is a result of the improved packing density. Similar investigations have been carried out by other workers [35, 41, 42] and they obtained the same type of results.

Fig. 3 shows X-ray diffraction patterns of titanium oxide coatings D.C. deposited on (100) silicon wafers. It is found that coatings deposited below 200 °C exhibit an amorphous structure. No crystallographic structure of TiO_2 (Rutile, Anatase or Brookite) is observed when the substrate temperature is too low. From 300 °C, small peaks begin to appear. Due to width and intensity of the diffracted signals, it can be said that coatings prepared at 300 °C are weakly crystallized but when temperature increases, several peaks can be observed showing the typical Anatase structure. This evolution can be attributed to an increase of the atoms diffusion at high temperature. Then, the film structure changes from amorphous to polycrystalline with substrate temperature. At 500 °C, a preferred orientation along (101) direction is chiefly observed. The well-developed Rutile structure has not been produced for this range of temperature but it can be obtained with an annealing treatment in air [25]. Therefore, Anatase to Rutile phase transition could be observed with substrate temperature higher than 500 °C. From previous studies [25, 43], for TiO_2 films made by sputtering, the amount of Rutile increases strongly when the temperature reaches 700 °C.

In order to compare D.C. and R.F. reactive sputtering, titanium oxide thin films have been deposited with a radio-frequency polarization at 13.56 MHz. Fig. 4 shows UV-visible transmission spectra of TiO_x coatings R.F. deposited on fused quartz for different substrate temperatures. The same deposition time has been used and about 3000 Å thick layers have been prepared. Less interference fringes are obtained compare

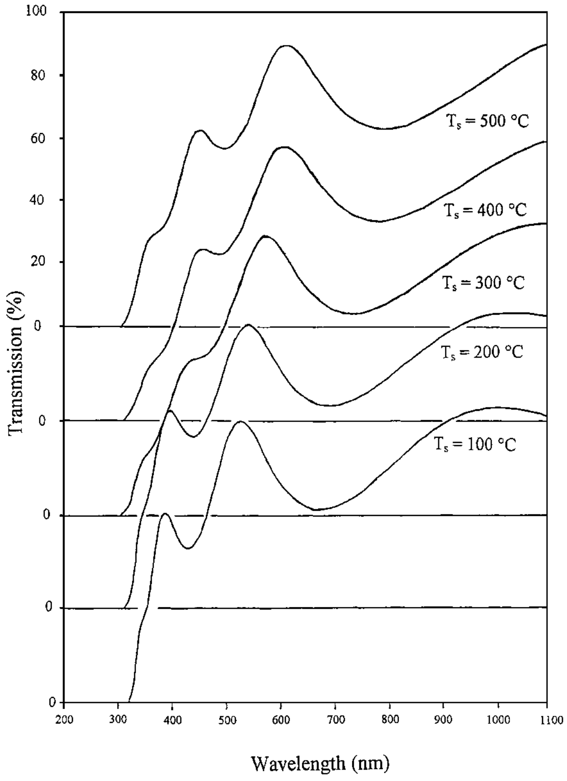

Figure 4 Optical transmittance in the visible region of titanium oxide coatings deposited at different temperatures with a R.F. polarization.

to Fig. 1 due to thinner coatings. As observed for TiO_x D.C. sputtered, the number of fringes decreases when the substrate temperature increases. So, deposition rate slowly decreases at high temperatures as observed previously. It is mainly due to a decrease of the particle condensation and an increase of the diffusion phenomenon. It is also interesting to see that minimum and maximum of the interference fringes are larger for coatings R.F. deposited. Evolution of the absorption band edge is clearly observed in Fig. 4. For titanium oxide coatings R.F. deposited up to 400 °C, it can be seen a shift to higher wavelengths. A reverse effect was noticed previously for TiO_x D.C. sputtered. This is not clearly explained but one can suppose that the morphology of the layers is strongly affected by the substrate temperature and so, it could be closely correlated to the shift of the absorption edge and also the decrease of the gap energy. When the temperature reaches 500 °C, the absorption edge is moved to lower wavelengths. This evolution can be linked to the crystallization effect observed from 500 °C in Fig. 6. This is not easily explained and other investigations, like deposition at high temperatures, could be helpful to better understand this phenomenon.

In Fig. 5, refractive indexes of R.F. deposited TiO_x coatings have been calculated with transmission spectra from the previous figure. The same effect observed for TiO_x films that have been D.C. prepared can be noticed when the substrate temperature increases. Therefore, titanium oxide materials deposited at high temperature have a more compact structure than those obtained with low temperature. This agrees with a changeover from porous films consisting of tapered crystallites separated by voids, to compact structure consisting of densely packed fibrous grains. In addition, if the refractive index of Anatase at $\lambda_{Na} = 589$ nm [44] is taken into account, the packing density P of the coatings can be calculated using the following formula [45]:

$$P = \frac{\rho_F}{\rho_B} = \frac{n_F^2 - 1}{n_F^2 + 2} \times \frac{n_B^2 + 2}{n_B^2 - 1}$$

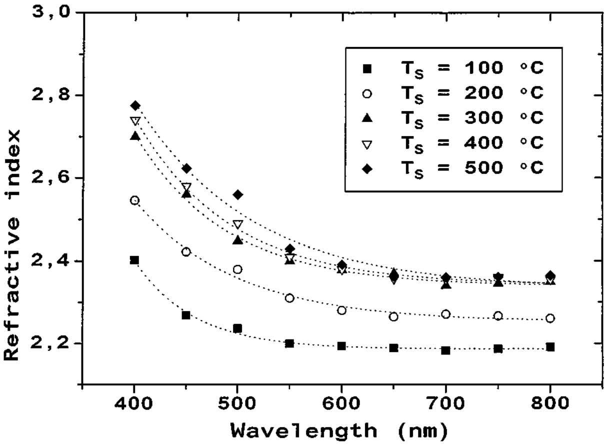

Figure 5 Refractive index of TiO_x coatings R.F. deposited on fused quartz. From Swanepoel's method, interference fringes observed from UV-visible transmission spectra have been used to calculate optical characteristics of the films. High refractive indexes are obtained when the substrate temperature reaches 300 °C.

TABLE I Optical and morphological properties of titanium oxide coatings R.F. or D.C. deposited for different substrate temperatures. The effect of the radio-frequency is clearly shown

	Substrate Temperature (°C)	100	200	300	400	500
D.C. Polarisation	Refractive index at $\lambda_{Na} = 589$ nm	2.126	2.136	2.147	2.188	2.204
	Packing density	0.85	0.86	0.86	0.88	0.89
	Deposition rate ($nm\,h^{-1}$)	310	310	305	305	270
R.F. Polarisation	Refractive index at $\lambda_{Na} = 589$ nm	2.193	2.294	2.373	2.392	2.416
	Packing density	0.88	0.93	0.96	0.96	0.97
	Deposition rate ($nm\,h^{-1}$)	200	200	190	180	180

with ρ_F = density of the film; ρ_B = density of the bulk (Anatase); n_F = refractive index of the film; n_B = refractive index of the bulk (Anatase).

The refractive index of Anatase ($n_{Ana} = 2.49$ at $\lambda_{Na} = 589$ nm) has been taken to be the refractive index of the bulk in the calculation of the packing density P. This has been determined for various substrate temperatures, and gives $P = 0.88$ at 100 °C and $P = 0.97$ at 500 °C (Table I). It is also interesting to see that the refractive index increases up to 400 °C and is nearly kept constant at higher temperatures. This can be correlated to the evolution of the absorption band edge and also to the crystallization phenomenon chiefly observed in Fig. 6. In fact, TiO_x material R.F. sputtered on (100) silicon wafers exhibit an amorphous structure up to 400 °C. At this temperature, small peaks begin to come out the background; these signals have been identified with positions corresponding to the Anatase structure. When the temperature increases again until 500 °C, single-phase Anatase is obtained and the preferred orientation along the (101) crystal planes is observed like TiO_x D.C. sputtered. One can suppose that at low substrate temperature, the as-deposited films are amorphous (or weakly crystallized) due to the low energy and the low mobility of particles impinging on the "cold" substrate. When the temperature increases, the first traces of long-range order appear mainly due to an augmentation of the surface diffusion which provokes organization of the materials.

3.2. Chromium oxide coatings

Optical properties of chromium oxide coatings are quite different from titanium oxide. They are also very sensitive to deposition parameters. As can be seen in Fig. 7, transmission spectra in the UV-visible region of chromium oxide coatings D.C. sputtered on quartz substrates at different temperatures have been recorded. Interference fringes previously obtained for TiO_x coatings are not observed for Chromium oxide layers. Dark brown colors have been seen for CrO_y coatings prepared at various temperatures. Then, Swanepoel's method used to calculate refractive index can not be applied to determine optical properties of chromium oxide. It can be only said that this material strongly absorbs the visible radiations. Moreover, weak oscillations can be distinguished for coatings at

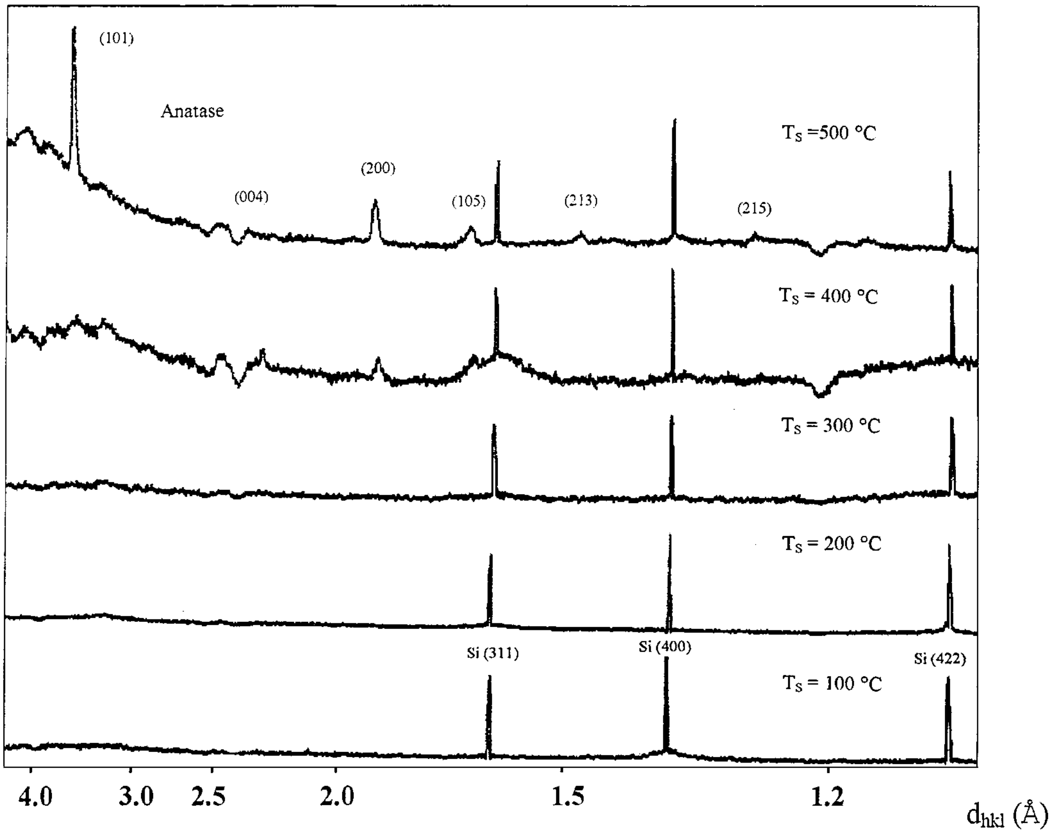

Figure 6 X-ray diffraction patterns of titanium oxide films R.F. deposited on (100) silicon wafers at different substrate temperatures. Anatase or amorphous structures can be prepared for this range of temperatures.

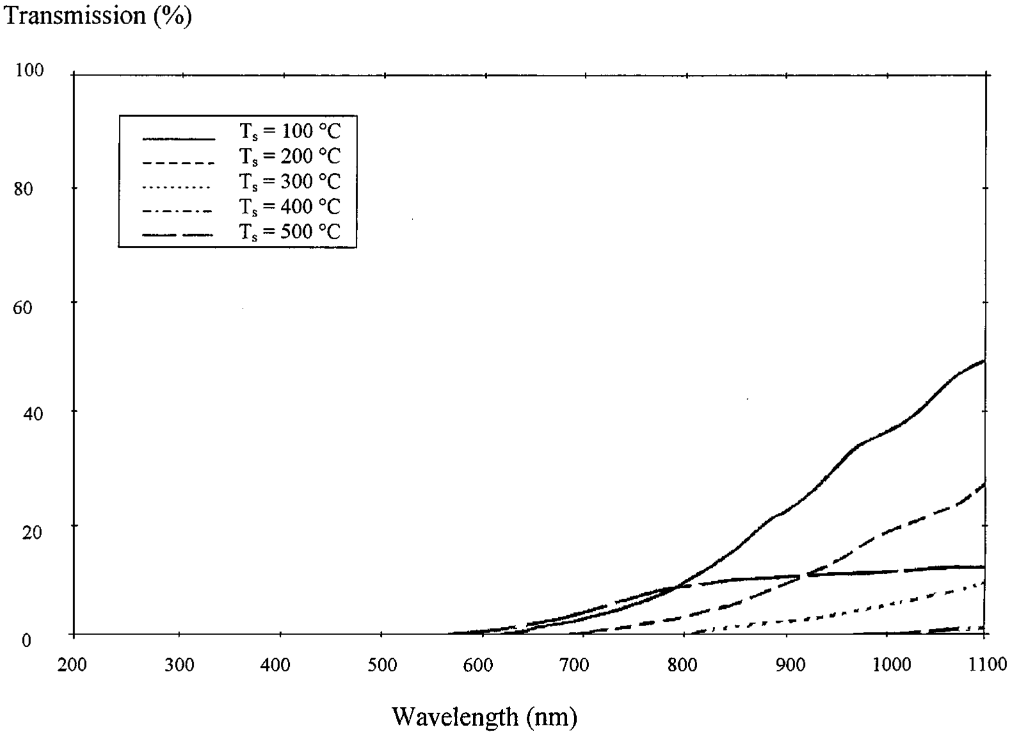

Figure 7 UV-visible transmission spectra of chromium oxide coatings D.C. sputtered on fused quartz at different substrate temperatures. No interference fringe can be observed.

100 °C. It should be interesting to record transmission spectra in the IR region because stronger interference fringes could be obtained and useful to calculate refractive index. It is also important to note that the absorption edge of CrO_y is not abrupt like TiO_x films and is shifted to higher wavelengths. It can be attributed to electronic properties and different types of optical absorption mechanisms between both materials.

The effect of the substrate temperature on the optical properties of CrO_y coatings is clearly illustrated by a decrease of the transmission when temperature increases up to 400 °C. One can suggest that the sticking probability of oxygen strongly depends on the surface temperature. In addition, an increase of the particle diffusion induces a release of the amount of oxygen. Then, the layers that become darker and darker may be due to a decrease of the oxygen in the material. In order to support this hypothesis, compositional analyses would be useful to determine the evolution of stoichiometry with the substrate temperature.

An interesting phenomenon is the evolution of transmission when the substrate temperature reaches 500 °C. An increase of the transmission and a shift to lower wavelengths is well observed. In addition, dark green coatings have been obtained for this temperature. If we take into account the crystallization effect observed at 500 °C in Fig. 9, it can be said that the transformation of optical characteristics of CrO_y coatings D.C. that are deposited are mainly due to some evolution of the crystallographic structure.

Transmission spectra of chromium oxide coatings that are R.F. sputtered have also been measured. From Fig. 8, materials do not exhibit clear interference fringes as observed previously and transmission is low due to dark brown layers. When the substrate temperature increases, transmission decreases and the absorption edge is also shifted to higher wavelengths like CrO_y D.C. sputtered. Then, the decrease of the optical properties does not depend on D.C. or R.F. polarization but is only a thermal effect. In addition, the increase of transmission observed for coatings that are D.C. deposited is also measured in Fig. 8 but the effect is more important. R.F. layers obtained at 500 °C exhibit a green color, brighter and more transparent than D.C. layers. Similar arguments as proposed previously can be used to explain the evolution of properties at high temperatures since crystallization of CrO_y coatings R.F. sputtered has been observed from 500 °C.

Fig. 9 shows X-ray diffraction patterns of chromium oxide coatings D.C. sputtered on (100) Si for different temperatures. It is found that all films deposited at low temperature (up to 400 °C) exhibit an amorphous structure. When the substrate temperature increases until 500 °C, the surface mobility of the sputtered particles increases as well and broad peaks with low intensity can be observed. Since crystallite size and width of the signal are closely linked, it can be said that CrO_y films are weakly crystallized. Comparison of the measured spectra with the powder diffraction file cards shows that chromium oxide Cr_2O_3 is obtained with a random orientation. The first traces or the long-range order have also been observed from 500 °C for CrO_y coatings R.F. deposited and Cr_2O_3 has also been produced. No clear difference has been noticed about the influence of D.C. or R.F. on the crystallization of chromium oxide films as it was observed for titanium oxide coatings. It should be interesting to deposit this material at higher temperature (above 500 °C) to study the effect of a D.C. and R.F. sputtering.

Concerning the temperature at which the materials begin to crystallize, it can be noticed that titanium oxide coatings crystallize at a temperature lower than chromium oxide. This is in agreement with the structural zone model proposed by Movchan and Demchishin [46] and Thornton [47], since melting point of Cr_2O_3 is higher than TiO_2 ($\text{m.p.}_{Cr2O3} = 2330\,°C$ and $\text{m.p.}_{TiO2} = 1840\,°C$ [44]). Therefore, for a substrate temperature of 500 °C, $T_S/T_{m.p.}$ is higher than 0.3 and the morphology of the coatings corresponds to the beginning of the zone 2 of the Thornton's diagram. The

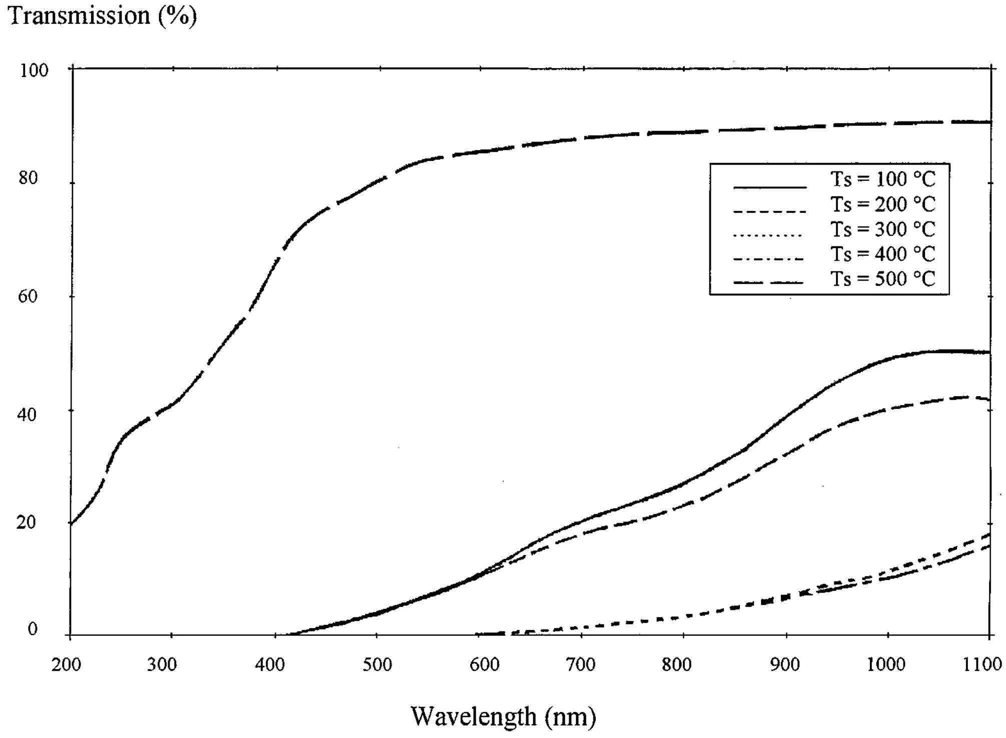

Figure 8 UV-visible transmission spectra of CrO_y coatings R.F. deposited on quartz. The effect of the substrate temperature is clearly illustrated. Up to 400 °C, transmission of the coatings slowly decreases.

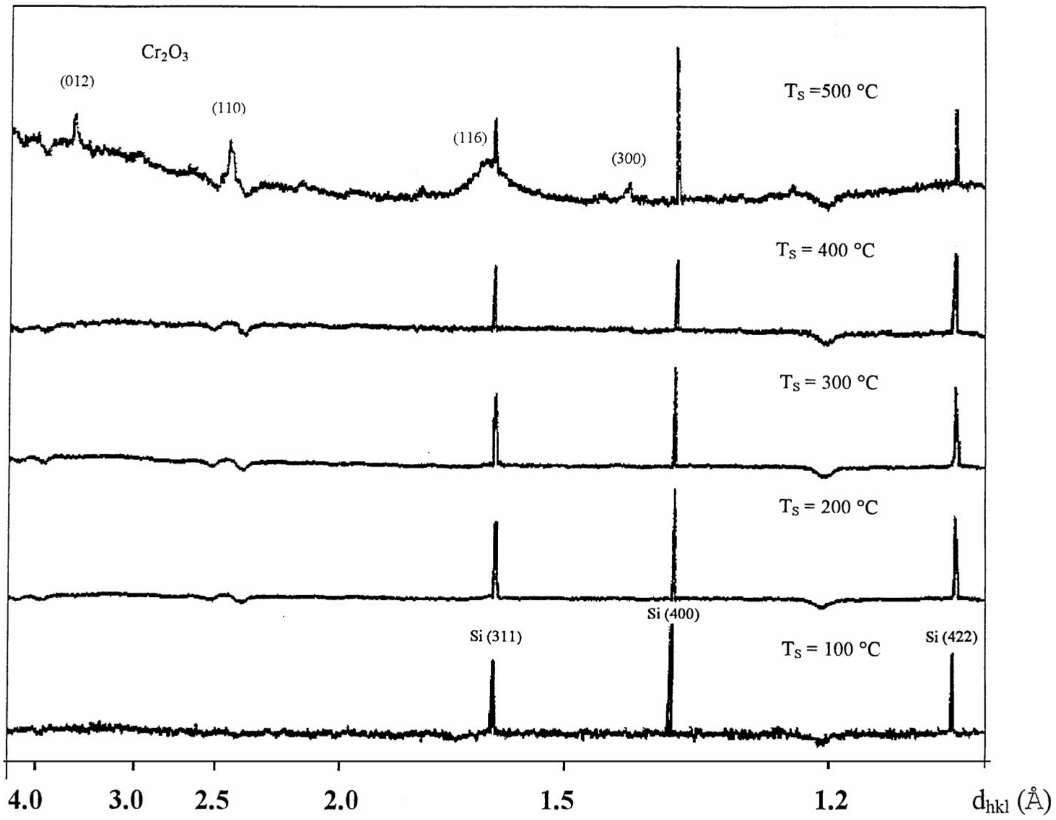

Figure 9 X-ray diffraction patterns of CrO_y coatings obtained from D.C. reactive sputtering on (100) silicon wafers. Layers prepared below 500 °C exhibit an amorphous structure and crystallization appears at high temperature.

microstructure, consists of columnar grains separated by dense intercrystalline boundaries.

3.3. Comparison between D.C. and R.F. sputtering

Titanium and chromium oxide coatings have been prepared from both types of polarization in order to show the main contrast that can be obtained between D.C. and R.F. reactive sputtering. In Figs 1 and 4, it can be seen that amplitudes of interference fringes are chiefly larger for TiO_x coatings R.F. deposited. In Fig. 10, refractive index of titanium oxide R.F. and D.C. deposited on quartz have been calculated for different temperatures. Coatings prepared with R.F. polarization exhibit higher refractive index for all substrate temperatures studied. Then, packing density of layers can be strongly improved using R.F. sputtering and high temperatures. This difference may be attributed to the alternation of the electric field for R.F. sputtering. In fact, with a R.F. polarization, during an alternation, the substrate and so the growing film is bombarded by electrons and also receives impingement of particles ejected from the target. One can suppose that particles can diffuse on the surface. This diffusion phenomenon may be improved by electronic bombardment which induces raising of the temperature. In D.C. sputtering, more voids are probably created because particles impinging on the substrate are rapidly or quasi instantaneously trapped by other particles coming from the target. Although R.F. sputtering ensures coatings have good optical and morphological properties, the deposition rates measured with D.C. polarization are always higher. An increase of the refractive index and so, of the packing density can be obtained if the films are deposited at high temperature nevertheless, density of the layers is chiefly increased with R.F. process. Therefore, this compromise must be taken into account between packing density and deposition rate.

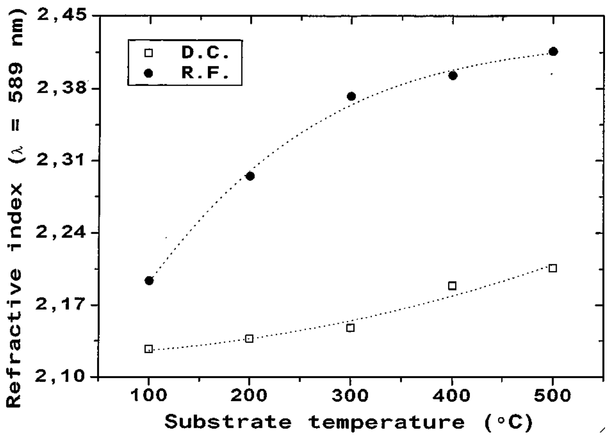

Figure 10 Refractive index at $\lambda_{Na} = 589$ nm of titanium oxide coatings prepared by D.C. and R.F. reactive magnetron sputtering on fused quartz. The influence of the substrate temperature clearly shows an increase of the index. The best optical properties are obtained with R.F. polarization and with high substrate temperatures.

It is also interesting to note that the crystallization phenomenon occurs at higher temperature for TiO_x coatings R.F. deposited. It is not clearly known why first traces of long-range order appear at lower temperature when materials are D.C. sputtered. Actually, no valid explanation has been found. It can be only suggested that the formation of crystal could be linked with a reverse relationship with the electronic bombardment of the substrate. Other investigations would be helpful to better understand these phenomena.

UV-visible transmission spectra of chromium oxide coatings D.C. and R.F. sputtered exhibit some contrasts. Transmission of CrO_y films R.F. deposited is always higher than D.C. materials for each substrate temperature. In addition at 500 °C, optical properties are quite different between D.C. and R.F. mode. R.F. sputtering exhibit more transparent CrO_y layers than D.C. sputtering. Considering a similar reasoning as previously, one can suppose that sticking coefficient of particles impinging on the substrate is diminished by the electronic bombardment due to the radio-frequency. So, high transmittance measured for CrO_y films R.F. prepared can be attributed to the effect of the alternation. It should be interesting to study the effect or the radio-frequency on some morphological properties of coatings and to investigate the influence of an electronic or ionic bombardment.

4. Conclusion

Titanium and chromium oxide thin films have been deposited by reactive magnetron sputtering. The effect of D.C. and R.F. polarization and the influence of the substrate temperature on some optical properties have been investigated. Deposition of TiO_x layers at high temperature showed that an increase of material density can be achieved. In addition, as-deposited coatings exhibited an amorphous structure and the crystallization phenomenon began to occur from 400 to 500 °C. Optical characteristics of CrO_y layers also showed a strong evolution with the substrate temperature especially at 500 °C, transparency and typical green color of chromium oxide have been observed. Cr_2O_3 phase has been determined at this temperature and amorphous coatings have been obtained at lower temperatures. The increase of diffusion on the surface of the substrate with temperature and the sticking probability on the substrate of oxygen particles have been suggested as the main parameters which can influence the evolution of optical and morphological characteristics. The differences between both materials have been noted and attributed to the difference of melting point.

Comparison between D.C. and R.F. reactive sputtering showed interesting results especially with regard to the evolution of optical properties and the packing density. Thin layers R.F. deposited exhibited better optical behaviors and denser structures than D.C. deposited. It has been proposed that the electronic bombardment of the substrate could increase the mobility of the particles impinging on the substrate and thus reduce voids in the films. Therefore, using R.F. polarization and an appropriate substrate temperature, morphological structure and porosity of the layers can be strongly improved.

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