Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 1151–1158

www.elsevier.com/locate/jeurceramsoc

# Sol–gel processing of $TeO_2$ thin films from citric acid stabilised tellurium isopropoxide precursor

A. Lecomte[a,*], F. Bamière[a], S. Coste[b], P. Thomas[b], J.C. Champarnaud-Mesjard[b]

[a] *Laboratoire "Science des Procédés Céramiques et de Traitements de Surface", UMR 6638 CNRS, ENSCI,*
*47–73, Avenue Albert Thomas, 87060 Limoges Cedex, France*
[b] *Laboratoire "Science des Procédés Céramiques et de Traitements de Surface", UMR 6638 CNRS,*
*Université de Limoges-Faculté des Sciences, 123–127, Avenue Albert Thomas, 87065 Limoges Cedex, France*

Available online 15 June 2006

## Abstract

A sol–gel process for $TeO_2$ thin layers synthesis was developed, including the tailoring of the tellurium alkoxide reactivity, their preparation by dip-coating and the effects of heat treatments on their structure and microstructure. High quality thin films were made by dipping silica glass substrates in solutions prepared in the tellurium isopropoxide, isopropanol, citric acid and water system. The structure and microstructure of the films were characterized by X-ray reflectometry, X-ray diffraction, optical and scanning electron microscopies as a function of the chemical parameters of the sol, withdrawal speed, temperature and time of annealing. They were found to be highly dependent on the initial thickness and applied thermal treatment. Indeed, $TeO_2$ thin films could be either quite fully dense and amorphous or made of randomly orientated $\gamma$-$TeO_2$ or/and $\alpha$-$TeO_2$ crystals. Firing at the highest tested temperature (~450–500 °C) promotes grain growth and islanding, so producing a layer of textured but isolated grains.

© 2006 Elsevier Ltd. All rights reserved.

*Keywords:* Sol–gel processes; Thin films; X-ray methods; Tellurium oxide

## 1. Introduction

Tellurium oxide-based materials have attracted considerable research interest in recent years due to their high refractive index, good non-linear optical properties and electrical semiconductivity appealing for many different applications.[1] Nevertheless, the limited success of practical exploitation of tellurite materials may be attributed to difficulties encountered in the synthesis of thin films that are required in optical and integrated electronic devices. Indeed, the processing of $TeO_2$-based glasses is generally performed by a conventional melting-quenching technique, which is well suited to produce bulk glasses[2] but inappropriate, to date, to produce thin films.

Among all methods of thin film synthesis, chemical or physical vapour deposition, pulverization, molecular beam epitaxy or laser ablation, the sol–gel processing offers an attractive route for the fabrication of such materials into devices. Moreover, its interest is unquestionable mainly because of its low cost, its easiness to control the synthesis parameters and the high precision in mixing different precursors for the fabrication of multicomponents oxides layers.[3,4]

The synthesis of high quality $TeO_2$-based thin films by either a dipping, spinning or spraying coating process requires the very high reactivity of tellurium alkoxides towards water to be solved. In a first step, a wide range of chemical modifiers[5,6] were investigated and found to be ineffective at retarding hydrolysis of tellurium alkoxides. Up to now, there have been very few reports on the successful production of high quality thin films from these precursors, although a study by Weng and Hodgson[7] did demonstrate that precipitation could be avoided by using a large amount of 1,2-propanediol and very low Te-alkoxide concentration and that thin films could be synthesised in a very limited composition range. More recently, the problems in use of tellurium(IV) alkoxides have been overcome by using, on the one hand, a tellurium(VI) complex precursor.[8] On the other hand, citric acid[9] was found to be the most efficient and suitable chemical modifier to control hydrolysis and condensation reactions of tellurium(IV) isopropoxide.

In the present work, we aim to show that citric acid is a relevant tellurium isopropoxide chemical modifier and par-

---

* Corresponding author. Tel.: +33 05 55 45 22 22; fax: +33 05 55 79 09 98.
*E-mail address:* a_lecomte@ensci.fr (A. Lecomte).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.05.029

ticularly promising for sol–gel thin films realisation. Tellurite thin layers are deposited on silica glass substrates by a dip-coating technique from sols prepared in the tellurium isopropoxide–isopropanol–citric acid and water system. Their structural and microstructural evolutions are investigated by X-ray reflectivity, X-ray diffraction, optical and scanning electron microscopies as a function of the chemical parameters of the sol, withdrawal speed, temperature and time of annealing. Corresponding gels and xerogels are also considered in a complementary way.

## 2. Experimental details

### 2.1. Sols, gels and films synthesis

All syntheses were performed in a glove box under dry air atmosphere. First, the tellurium isopropoxide ($Te(OCH(CH_3)_2)_4$, purity >99.9%, Alfa-Aesar) was diluted in anhydrous isopropanol (purity >99%, Prolabo) to give a 1 mol/L solution. Second, citric acid was dissolved in a mixture of this solution and anhydrous isopropanol with appropriate amounts in order to reach the desired alkoxide concentration $C$ and modification ratio $R$ = [citric acid]/[Te-alkoxide] at the end of the synthesis. Finally, a solution of water diluted in isopropanol was added drop-wise under vigorous mechanical stirring. Each precursor sol was identified by its alkoxide concentration, $C$, modification ratio, $R$, and hydrolysis ratio $W$ = [water]/[alkoxide]. In this work, $W$ was generally kept equal to 4, the stoichiometric quantity to fully hydrolyse the Te-isopropoxide. These homogeneous, clear and transparent sols were used either for gels or thin films synthesis.

In the former case, the glass vessel was hermetically closed and kept at room temperature or 60 °C until gelation occurred. The gelation time was defined by observing the gel surface stiffness after tilting the sol container from time to time, the interval between two observations being obviously related to the expected gel time. We assume that the sol is gelled when the surface remains absolutely flat during tilting, i.e., with no deformation. According to the drastic changes of the gel time with the citric acid ratio as well as the alkoxide concentration, such simple method is accurate enough for gel time determination.

In the latter case, the coating of tellurium oxide precursor films was carried out just after the sol synthesis using a dipping-withdrawing method under ambient conditions. Polish mirror silica-based glass (Vycor: 96 mol% $SiO_2$–4% $B_2O_3$, Goodfellow, France) was used as coating substrates. The withdrawal speed was ranging from 1 to 200 mm/min.

The xerogels as well as the dried films were then fired in an electric furnace at a rate of 5 °C/min up to the desired temperature and for the chosen annealing time. The first steps of thermal evolution of the films were analysed from a single thin film undergoing a "cumulative heat treatment", i.e., the firing of the sample was stopped in step of 50 °C from 20 up to 550 °C, the sample was air quenched and then successively characterized by X-ray reflectivity, X-ray diffraction and microscopy before being reintroduced into the furnace at the same temperature for the continuation of the annealing. Xerogels were also investigated by using differential scanning calorimetry (DSC) coupled with thermogravimetry (TG) and performed from 20 to 550 °C with a heating rate of 10 °C/min under air atmosphere using a Netzch STA 409 instrument.

### 2.2. X-ray experimental set-ups

The tellurium oxide thin films were examined by X-ray reflectivity (XRR). The data were collected by using an original angular dispersive reflectometer[10] initially developed by Naudon et al.[11] All reflected beams were simultaneously recorded by using a linear position sensitive detector (INEL LPS 50). As no movement of both the sample and the detector was necessary during the measurement, the exposure time necessary to data recording was obviously considerably reduced, typically about 4 h. The microstructural parameters such as thickness, X-ray refractive index and both surface and interface roughness (rms), as defined by Nevot et al.,[12] were obtained by fitting the experimental data by using the well-known Parratt formalism.[13] In the range of the X-ray radiation, we recall that the index of refraction is complex and commonly written[14]:

$$n = 1 - \delta - i\beta \tag{1}$$

with

$$\delta = \frac{r_e\lambda^2}{2\pi} N_a \rho \frac{\sum_i n_i (Z_i + f_i')}{\sum_i n_i A_i} \tag{2}$$

and

$$\beta = \frac{r_e\lambda^2}{2\pi} N_a \rho \frac{\sum_i n_i f_i''}{\sum_i n_i A_i} \tag{3}$$

where $r_e$ is the classical electron radius, $r_e = 2.818 \times 10^{-15}$ m, $N_a$ the Avogadro number, $\lambda$ the wavelength of X-rays and $\rho$ is the material density. $Z_i$, $f_i'$, $f_i''$, $n_i$ and $A_i$ are respectively the atomic charge, the real and imaginary parts of the anomalous dispersion terms,[15] the atomic fraction and the atomic mass of species $i$ composing the material. The real part of the refractive index is characteristic of the refraction whereas the imaginary part is characteristic of the absorption. The values $\delta$ and $\beta$ are very small and typically of the order of $10^{-4}$ to $10^{-8}$. Consequently, the real part of the refractive index being smaller than 1, the total reflection of X-rays is observed for incidence angles below a critical angle $\alpha_c$, which is defined by $\alpha_c = \sqrt{2\delta}$ if absorption is negligible.

X-ray diffraction was used to determine the crystalline phases after heat treatment. The diffractometer consists in a Debye–Scherrer-like set-up, operating on flat samples, fitted with a forward quartz monochromator (Cu $K_{\alpha 1}$ radiation) and a curve position sensitive detector (CPSD INEL, 120° angular aperture) allowing the diffracted peaks to be simultaneously recorded.[16] This asymmetric geometry under controlled and fixed incidence is particularly suitable for surface characterization and thin film structure analysis. The incidence angle $\omega$ was fixed to about 3–7° in order to favour the irradiated volume of the layer without impairing the resolution, i.e., without an excessive broadening of the X-ray diffraction line profile. To evidence preferred crystallographic orientations, XRD patterns were also performed in symmetric configuration, i.e., by setting the incidence beam angle $\omega$ exactly to the Bragg angle $\theta_{hkl}$ of the Bragg peak of the $TeO_2$ phase under consideration.

## 3. Results and discussion

From the standpoint of gelation study, the alkoxide concentration $C$ was varied between 0.05 and 0.9 mol/L while the modification ratio $R$ was ranging from 0 to 2, $W$ being kept equal to 4. The precursor sols evolution at room temperature (about 20 °C) was so low that the gelation study was then systematically conducted at 60 °C. The final state of the gels was first assessed according to homogeneity, transparency and mechanical rigidity.

For $0 < R < 0.3$ and whatever the value of $C$, precipitation always occurred as soon as the water–isopropanol mixture was added. For large modification ratios, $R > 1.2$, gelation did not occur and precipitation was also observed after an incubation time depending on $C$. For $0.3 < R < 1.2$, the final products were gels that differed according to $C$. Near the precipitation boundaries or for the highest concentrations, $C > 0.7$ mol/L, the gels were inhomogeneous and became turbid. For $0.1 < C < 0.7$ mol/L, very homogeneous and transparent gels were synthesised with a very good rigidity. When the alkoxide concentration was decreased to about $C = 0.1$ mol/L, the gels turned soft. Below this limit, a phase separation was noticed and the samples were composed of a very soft gel surrounded with a liquid phase. As generally observed for sol–gel chemistry,[3] the gelling time $t_g$ for a given concentration, increases drastically when the modification ratio increases. In the same way, for a given $R$, $t_g$ decreases when $C$ is increased. For example, with $C = 0.5$ mol/L and $W = 4$, this gelling time ranges from 0.25 to 200 h for $R = 0.4$ and 1, respectively.

From these macroscopic observations, a major finding was that citric acid is a relevant Te-isopropoxide chemical modifier. For a better understanding of the basic reactions involved in the gelation process, a complementary study[9] by using Fourier transform infra red spectroscopy (FTIR) and small angle X-ray scattering (SAXS) has been carried out. The FTIR investigation has evidenced that citric acid is strongly bonded to Te-isopropoxide, slowing down the hydrolysis and condensation reactions. From the standpoint of SAXS measurements, the gelling network is always made of interconnected fractal aggregates, constituted of very small Te-rich elementary particles of 2–3 nm in diameter. The elementary particles are instantaneously formed when the water is added and their size and number do not evolve during the gelation. The fractal aggregates result from their hierarchical aggregation according to a reaction limited cluster aggregation mechanism. Whatever the citric acid ratio, the fractal dimension of the aggregates remains constant at about 2.1 in spite of the sticking probability variation. Consequently, the microstructure of the gels is self-similar for a wide range of alkoxide concentrations and only differs from their fractal aggregate size which decreases when the tellurium isopropoxide concentration increases. These results as well as the phase diagram previously summarized have been described in details elsewhere.[9]

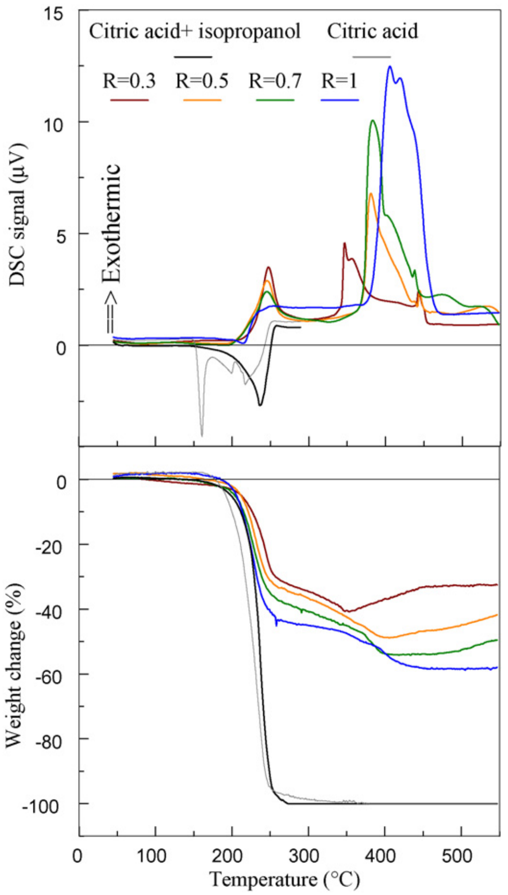

Fig. 1. DSC and TG results of citric acid, a mixture of citric acid and isopropanol and xerogels synthesized from precursor sols which chemical parameters are $C = 0.5$ mol/L, $W = 4$ and various complexing ratio $R$.

The xerogels are obtained by drying these gels at 60 °C and then 100 °C for 24 h, an intermediate grinding being processed. Their decomposition process, under air atmosphere, was investigated by DSC, TG and XRD. In Figs. 1 and 2 are respectively displayed the thermal analysis and X-ray diffraction results of the xerogels synthesised with a fixed concentration, $C = 0.5$ mol/L, located in the centre of the transparent, homogeneous and mechanically rigid gels domain, and various complexing ratios $R$. After drying, all xerogels are amorphous.

Whatever the complexing ratio $R$, the DSC and TG curves as well as the crystallisation sequence of the $TeO_2$ phases exhibit the same feature except for a slight temperature shift. At heat treatment temperatures between 200 and 280 °C, DSC and TG results show an exothermic peak which height decreases when $R$ increases. This process associated to a large weight loss, from 30 to 47%, may be attributed to the combination of evaporation and combustion of un-reacted citric acid and organic components. This organic groups decomposition leads to the occurrence of a partial reduction of the hydrolysis products to form metallic tellurium as revealed by XRD. As the temperature is increased, several exothermic processes overlap leading to their unambiguous attribution rather difficult. Nevertheless, accordingly to the

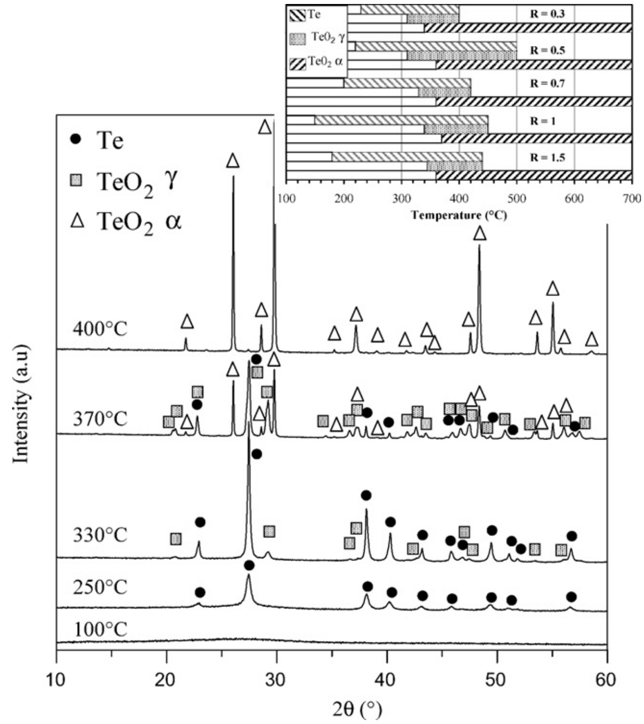

Fig. 2. X-ray diffraction patterns of xerogels synthesized from a precursor sol which chemical parameters are $C = 0.5$ mol/L, $W = 4$, $R = 0.7$ and fired at various temperatures from 100 up to 400 °C for 1 h. In the inset, phases existence domains as a function of the annealing temperature and complexing ratio $R$.

XRD patterns, they may be successively attributed to the crystallisation of γ-$TeO_2$, to the combustion of organic components as suggested by a lower continuous weight loss, about 10–15%, then to the progressive transformation of γ-$TeO_2$ into the α-$TeO_2$ phase and finally to the α-$TeO_2$ crystallisation. Finally, a slight increase of weight for the highest temperatures is due to the oxidation of metallic tellurium since XRD patterns exhibit its disappearance.

The visual observations of the xerogel powders treated at various temperatures between 100 and 550 °C have finely corroborated the DSC and XRD results. They have shown that the powders underwent three distinct changes on heating. The xerogel colour changed from being initially white powders to more or less dark brown/black for moderate temperature heat treatments, followed by a progressive brightening after further increase of the annealing temperature and finally leading to recover white colour powders. These features were similar in each xerogel powder, although the temperatures and occurrence of the darkening and brightening were dependent upon the xerogel composition, i.e., upon the citric acid ratio and alkoxide concentration. Therefore, these colour changes correspond respectively to the initial amorphous state prior to heat treatment, followed by the formation of crystalline Te metal with subsequent crystallisation of $TeO_2$ polymorphs at higher temperatures.

The formation of metallic tellurium as dark precipitates on heating sol gel precursors has been previously reported in a number of studies.[5–9,20] The ensuing development of γ-$TeO_2$ crystals, which may act as nucleation sites for the subsequent growth of α-$TeO_2$ crystals, has been suggested to occur from the oxidation of previously formed rich metallic tellurium domains.[20] However, the appearance of γ-$TeO_2$ phase directly from the amorphous precursor cannot be totally ignored. Such low temperature crystallisation as well as the well-known poor glass former ability of tellurium oxide in its pure form prevent the amorphous xerogel to $TeO_2$ glass conversion which will be more or less detrimental or beneficial depending upon the aimed material application.

The thin films synthesis conditions have been deduced from the FTIR, SAXS, XRD, xerogels thermal analysis and gelation studies. In the one hand, the complexing ratio $R$ has to be high enough to avoid precipitation during substrate withdrawal. In the other hand and in combination with water content, it has to be as low as possible to prevent metallic tellurium crystallisation. Thus, the complexing ratio $R$ of the precursor sol was kept in a rather limited range from 0.5 to 0.7 and $W$ being generally equal to 4. Then, the coatings deposited on vycor glass wafers have been synthesised from various Te-isopropoxide sol concentrations $C$ ranging from 0.1 to 0.5 mol/L and withdrawal speeds. After a drying at 100 °C, the films are transparent, continuous, homogeneous and crack free as observed by optical microscopy.

The experimental X-ray reflectivity curves recorded for the uncovered vycor substrate and for the as prepared coatings are plotted in Fig. 3, the solid lines corresponding to the best fit of the Parratt model function. The intensity of the reflected beam by the vycor substrate shows a classical evolution of the reflected intensity versus the incidence angle $\alpha$ for a dioptre separating two media of different electronic densities. The measured critical angle corresponding to total reflection, $\alpha_c = 0.21°$, is in very

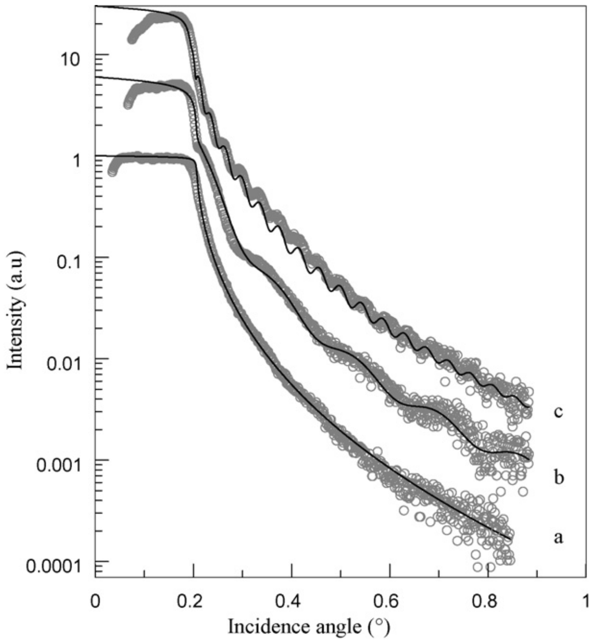

Fig. 3. Withdrawal speed dependence of the X-ray reflectivity curves for as prepared thin films coated on silica glass wafer (a) from a precursor sol with $C = 0.1$ mol/L, $R = 0.5$, $W = 4$ and at withdrawal speed of 10 mm/min (b) and 100 mm/min (c). Curves are arbitrary vertically shifted for clarity. Experimental points (symbols) are well fitted by using the recursive Parratt formalism (lines).

good agreement with the theoretical value of 0.216° and the root means square roughness is about 0.8 nm.

The reflected intensity curves obtained from the as prepared layers present oscillations (Kiessig fringes) which are significant of continuous, homogeneous and uniform layers.[17] From the simulations, the layer microstructural parameters, its thickness, refractive index and roughness have been deduced.

For a Te-alkoxide concentration $C$ fixed at 0.1 mol/L, the thickness of the dried layers increases, accordingly to the Landau–Levich law,[3] from about 26 to 97 nm when the withdrawal speed is varied from 10 to 100 mm/min, respectively. The rather weak depth of the Kiessig fringes collected for these raw coatings is due to their refractive index which is quite close to the substrate one. The root means square roughness parameters, measured for each interface, are lower than 1 nm and in the same range than the one of the substrate, such low values attest of the good quality of the sol–gel $TeO_2$-based layers. In the same way, their thickness has been also varied by managing the alkoxide concentration. For example, it evolves from 26 to 105 nm for $C = 0.1$ and 0.5 mol/L, respectively, the withdrawal speed being fixed at 10 mm/min.

We turn now to the thermal evolution of these layers. The thermal evolution of the thin films microstructure has been investigated on a single thin film coated at a withdrawal rate of 100 mm/min from a sol with the following composition: $C = 0.1$ mol/L, $R = 0.5$ and $W = 4$. Then, the resulting sample has been fired with the "cumulative heat treatment" up to 500 °C, as described in the experimental part.

The experimental X-ray reflectivity curves recorded after each thermal treatment are plotted in Fig. 4. As the temperature increases, the position of the critical angle as well as the period of the interference fringes continuously increase. The corresponding thicknesses, $\delta$ and $\beta$ values of the refractive index deduced from the simulations with the Parratt model are displayed in Fig. 5.

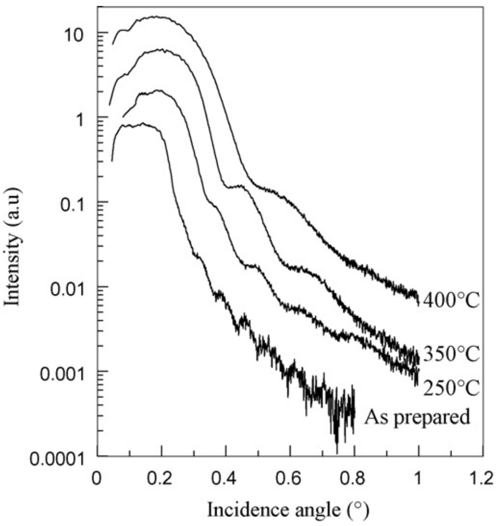

Fig. 4. X-ray reflectivity curves for a $TeO_2$-based thin film coated at a withdrawal speed of 100 mm/min on silica glass wafer from a precursor sol with $C = 0.1$ mol/L, $R = 0.5$, $W = 4$ and fired using a cumulative thermal heat treatment up to 400 °C. Curves are arbitrary vertically shifted for clarity.

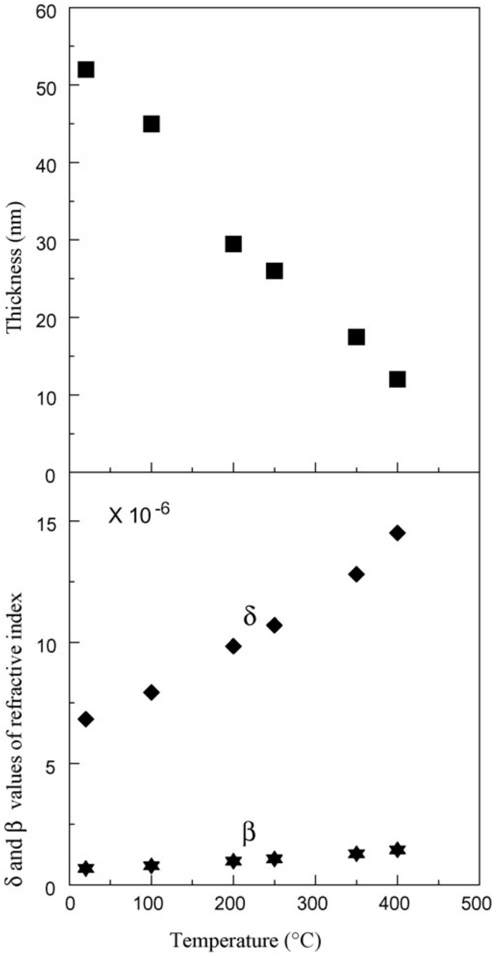

Fig. 5. Firing temperature dependence of the thickness, $\delta$ and $\beta$ parameters of the layer refractive index as deduced from the X-ray reflectivity curves for a $TeO_2$-based thin film coated on silica glass wafer from a precursor sol with $C = 0.1$ mol/L, $R = 0.5$, $W = 4$ and at withdrawal speed of 100 mm/min.

The layer thickness continuously decreases from 52 to 12 nm for the as prepared film and for the 400 °C point, respectively. Concomitantly, the $\delta$ and $\beta$ parameters of the layer refractive index increase and reach respectively $1.45 \times 10^{-5}$ and $1.44 \times 10^{-6}$ values at 400 °C. The relative density of the film can be deduced from the XRR curves by comparing the $\delta$ and $\beta$ values to the theoretical ones[15] for dense $\gamma$-$TeO_2$ ($\delta = 1.567 \times 10^{-5}$ and $\beta = 1.570 \times 10^{-6}$) and $\alpha$-$TeO_2$ ($\delta = 1.641 \times 10^{-5}$ and $\beta = 1.644 \times 10^{-6}$) phases.

Thus, at 400 °C, the layer appears quite dense with about 90% of the theoretical density of $\alpha$-$TeO_2$ phase. On the one hand, the densification of the layer has to be related to the removal of residual organics initially contained in the coating in agreement with the xerogels thermogravimetry analysis. On the other hand, this densification occurs by a one dimensional shrinkage, i.e., by a strong reduction of the thickness in a similar way as previously mentioned for other layer systems with various chemical compositions.[18,19] Once again, the root means square roughness parameters, measured for each interface, are in the same range than the roughness of the silica glass substrate and attest to the quality of the sol–gel layers even after a thermal treatment. From the standpoint of XRD, no diffraction peaks are detected accordingly to the very low layer thickness and the scattering by the amorphous substrate.

With a further increase of the temperature of heat treatment up to 500 °C, the coating breaks up into isolated islands leading to the disappearance of the Kiessig fringes from the XRR curves. Two families of islands are distinguished on optical microscopy micrographs (Fig. 6). The islands of the first family exhibit acicular shape whereas the second ones have puck-like profile. When the annealing time at 500 °C is increased up to 3 h, the islands thicken up and reduce their size in the plane to result in a sugar loaf shape as observed on SEM micrographs (Fig. 6).

During this break-up process, the crystallisation of the thin films has shown some differences to the bulk xerogels. In fact, XRD patterns have evidenced the development of highly preferred orientation which could be identify by performing the XRD patterns in symmetric configuration, i.e., by setting the incident X-ray beam angle $\omega$ exactly equal to the Bragg angle $\theta_{hkl}$ of the Bragg peak of the $TeO_2$ phase under consideration.

Since 450 °C, the first and unique diffracted peak that appears is located at an angle $2\theta$ about 28.8° (Fig. 7). This Bragg peak is unambiguously assigned to the (1 1 1) $\alpha$-$TeO_2$ crystallographic planes which are lying parallel to the substrate surface. With the further increasing of annealing temperature or time, a second diffracted peak, located at an angle $2\theta$ about 19.2°, is revealed (Fig. 7). In previous reports,[7,20] it was assigned to the paratellurite (1 0 0) planes which have a calculated diffraction angle of 18.4° in $2\theta$. Unfortunately, this reflection does not exist for the $P4_12_12$ space group of $\alpha$-$TeO_2$ as mentioned in the 42–1365 JCPDS file. We may explain this Bragg peak by assuming that the low layer thickness and the large discrepancy between the thermal dilatation coefficients of silica glass substrate and $TeO_2$ phases may induce constraints in islands. Such constraints could change the cell parameters as well as the crystalline symmetry. Three space groups with a quadratic symmetry are then conceivable: the $P422$, $P4_122$ and $P222$. Nevertheless, in regards with the very low number of diffraction peaks, it is rather difficult to solve the problem. Such islanding and highly preferred orientation are in good agreement with the

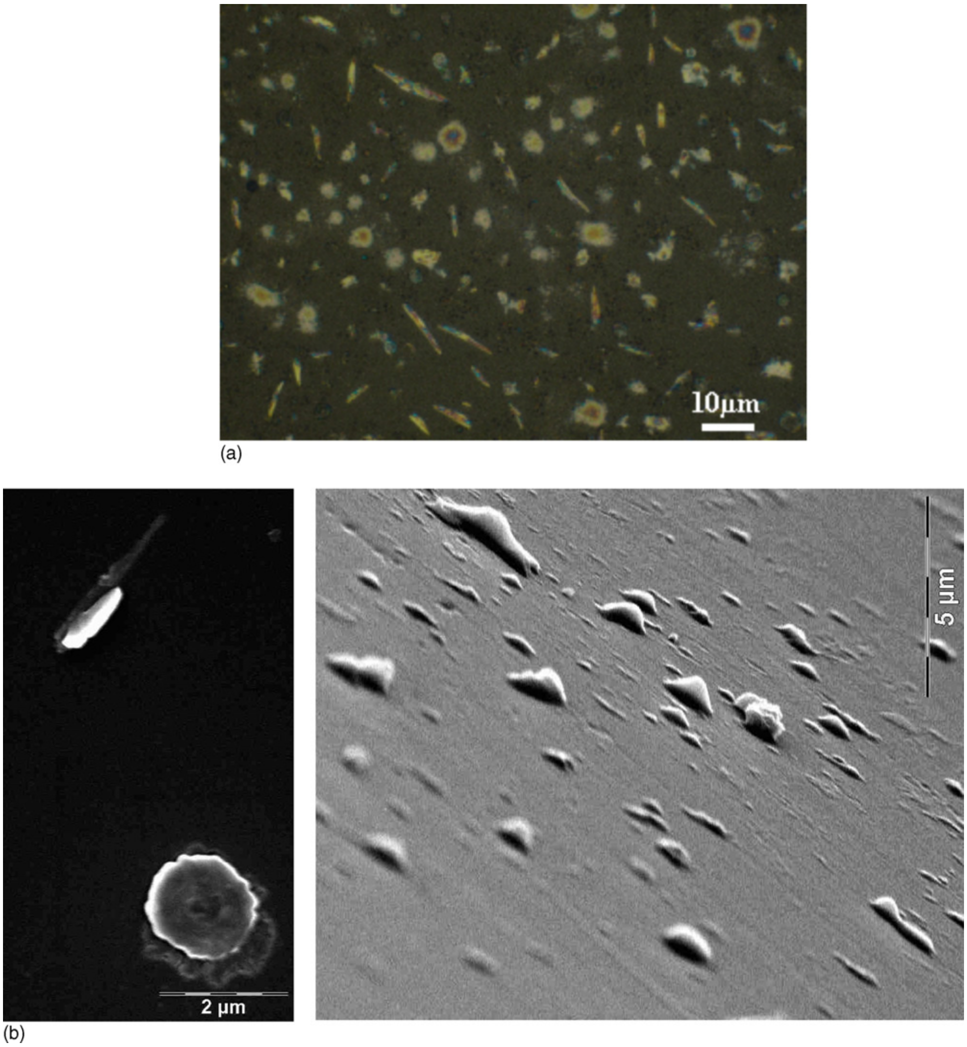

Fig. 6. Optical and SEM micrographs of the thin film coated on silica glass wafer from a precursor sol with $C = 0.1$ mol/L, $R = 0.5$, $W = 4$ and at withdrawal speed of 100 mm/min after heat treatment at 500 °C for 0.5 h (a) and 3 h (b) of annealing time.

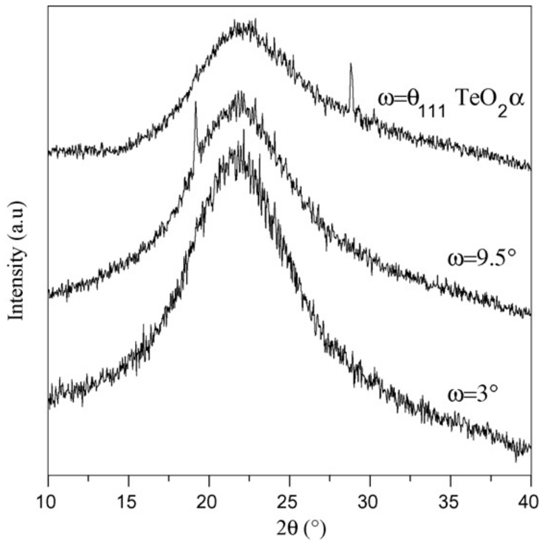

Fig. 7. Symmetric and asymmetric XRD patterns of the thin film coated on silica glass wafer from a precursor sol with $C = 0.1$ mol/L, $R = 0.5$, $W = 4$, at withdrawal speed of 100 mm/min and after heat treatment at 500 °C for 0.5 h.

observations carried out on similar[7,20] and chemically diverse systems.[21,22]

Thicker layers were also investigated. They were synthesised by increasing the Te-alkoxide concentration in the precursor sol. Thus, a new thin film was coated at a withdrawal rate of 100 mm/min from a sol with the following composition: $C = 0.5$ mol/L, $R = 0.7$ and $W = 4$. The resulting layer thickness was about 450 nm as estimated by the Landau–Levich law. To avoid islanding, the firing temperature was adjusted to 400 °C and the annealing time was varied from 0 to several hours.

X-ray diffraction measurements show that the thermal treatment induces first the crystallisation of the metallic tellurium. This phase totally disappears due to its oxidation for annealing time as short as 30 min (Fig. 8). Increasing the annealing time results in a rapid apparition of γ-$TeO_2$ phase and then to the progressive apparition of α-$TeO_2$ phase. During the thermal treatment, the amorphous film is transformed in a polycrystalline layer with a random orientation of either metallic tellurium, γ-$TeO_2$ or α-$TeO_2$ crystals, the relative intensities of the metallic tellurium, γ-$TeO_2$ and α-$TeO_2$ peaks being in good agreement with JCPDS files, respectively. As the different $TeO_2$ phases appear successively and without coexistence, we can choose the crystalline phase in which the film could be transformed by optimising the thermal treatment.

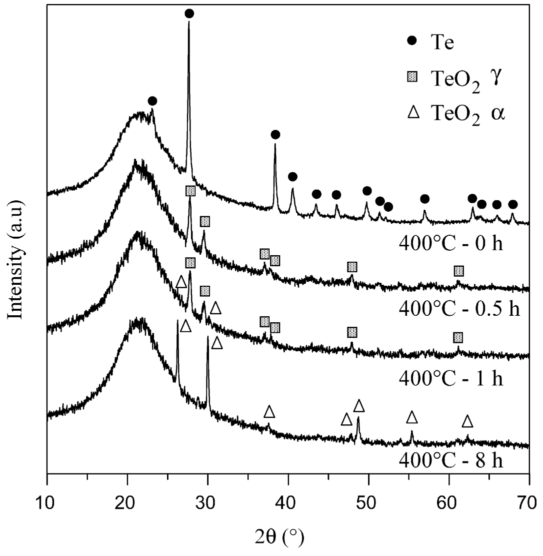

Fig. 8. X-ray diffraction patterns of a thick layer synthesized from a precursor sol which chemical parameters are $C = 0.5$ mol/L, $W = 4$, $R = 0.7$, at withdrawal speed of 100 mm/min and fired at 400 °C for various annealing times.

At this stage, the film–substrate interface does not seem to influence the layer microstructural evolution and the layer evolves as a bulk xerogel. Indeed, during the dipping, the liquid film runs out on the substrate, adheres to its surface and the evaporation of solvents leads to its rapid solidification. The as prepared layer could be considered as a xerogel obtained by a concentration effect. The visual observations of the thin films annealed at various temperatures between 100 and 550 °C have been also corroborated by this conclusion as well as the bulk xerogel colour evolution on heating and thin films XRD results. The thin film appearance changed from being initially transparent to appear with a metallic brilliance like a mirror for low temperature heat treatments, followed by a progressive brightening of the dark brown colour after further increase of the annealing temperature and finally leading to recover their transparency as long as the islanding stage is not reached.

These features were similar in each thin film, although the temperatures, the occurrence of the darkening and the speed of brightening were mainly dependent upon the thin film thickness in agreement with previous studies.[5,7,20] Therefore, these thin film colour changes correspond respectively to the initial amorphous state prior to heat treatment, followed by the formation of crystalline Te metal with subsequent crystallisation of $TeO_2$ polymorphs at higher temperatures due to the metallic tellurium oxidation. The thin film darkening is a short-lived transient stage and appears as a minor drawback. Indeed, the optical transparency is easily and rapidly recovered concomitantly to the oxidation of metallic tellurium by optimizing the temperature and time of annealing.

With regard to all these results, the sol–gel thin film synthesis appears to be a valuable alternative route to the physical processed layers.[23,24]

## 4. Conclusion

Citric acid has been evidenced to be a relevant tellurium isopropoxide chemical modifier leading to the successful management of hydrolysis-condensation reactions and thin films synthesis by a sol–gel route. The layers, synthesized on silica glass substrate by a dip-coating process, are continuous, homogeneous, crack free and exhibit good quality of both surface and interface states. Their nanometric thicknesses are easily managed through the Te-alkoxide sol concentration as well as the withdrawal speed.

The structure and microstructure of the films were found to be highly dependent on the initial thickness and applied thermal treatment. Indeed, the thinner $TeO_2$ films are quite fully dense and amorphous. Their firing at the highest tested temperature (∼450–500 °C) promotes islanding, so producing a layer of textured but isolated grains. The microstructure of the thicker $TeO_2$ coatings evolves as the one of the corresponding bulk xerogel. At this stage, the layer–substrate interface does not seem to influence the microstructure of the amorphous thin film which is transformed in a polycrystalline layer with a random orientation of either metallic tellurium, $\gamma$-$TeO_2$ or $\alpha$-$TeO_2$ crystals.

Although these results strongly suggest that sol–gel processing is a very interesting and potential process route to synthesize $TeO_2$-based materials and thin films and may offer a lower cost alternative to the evaporation and sputtering techniques, its recurrent drawbacks, i.e., precursor crystallization prior to glass formation and short-lived darkening due to metal tellurium crystallization, have to be solved. As the high Te-isopropoxide reactivity toward water is fixed by using citric acid, the future required work to improve the thermal stability and optical properties of the resultant thin films will be aimed at appropriate composition changes in the precursor sols, like addition of oxidizing agents, as well as by varying the atmosphere, temperature and time of annealing.

## References

1. El-Mallawany, R. A. H., *Tellurite Glasses Handbook: Physical Properties and Data*. CRC Press, Boca Raton, Florida, 2001.
2. Dutreilh-Colas, M., Nouveaux matériaux pour l'optique non linéaire: synthèse et étude structurale de quelques phases cristallisées et vitreuses appartenant aux systèmes $TeO_2$–$Tl_2O$–$Ga_2O_3$ et $TeO_2$–$Tl_2O$–PbO. Thesis, University of Limoges, France, 2001.
3. Brinker, C. J. and Scherer, G. W., *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*. Academic Press, New York, NY, 1990.
4. Livage, J., Sanchez, C. and Babonneau, F., Molecular precursor routes to inorganic solids. In *Chemistry of Advanced Materials: An Overview*. Wiley-VCH, New York, NY, 1998.
5. Hodgson, S. N. B. and Weng, L., Preparation of tellurite thin films from tellurium isopropoxide precursor by sol–gel processing. *J. Non-Cryst. Solids*, 2000, **276**, 195–200.
6. Coste, S., Thomas, P., Lecomte, A., Champarnaud-Mejard, J. C., Guinebretière, R. and Dauger, A., Preparation of $TeO_2$-based materials by the sol gel process. *Phys. Chem. Glasses*, 2002, **43C**, 405–408.
7. Weng, L. and Hodgson, S. N. B., Sol–gel processing of tellurite materials from tellurium ethoxide precursor. *Mater. Sci. Eng.*, 2001, **B87**, 77–82.
8. Weng, L., Hodgson, S. N. B., Bao, X. and Sagoe-Crentsil, K., Achieving controllable sol–gel processing of tellurite glasses through the use of Te(VI) precursors. *Mater. Sci. Eng.*, 2004, **B107**, 89–93.
9. Coste, S., Evolution structurale et microstructurale de précurseurs d'oxyde de tellure élaborés par voie sol–gel. Thesis, University of Limoges, France, 2003.
10. Lenormand, P., Etude de l'évolution microstructurale de précurseurs d'oxyde de zirconium à l'état de gel, xérogel, couche mince et aérogel par diffusion de rayons X. Thesis, University of Limoges, France, 2001.
11. Naudon, A., Chihab, J., Goudeau, P. and Mimault, J., New apparatus for grazing X-ray reflectometry in the angle resolved dispersive mode. *J. Appl. Cryst.*, 1989, **22**, 460–467.
12. Nevot, L., Pardo, B. and Corno, J., Characterization of X–UV multilayers by grazing incidence X-ray reflectometry. *Rev. Phys. Appl.*, 1988, **23**, 1675–1686.
13. Parratt, L. G., Surface studies of solids by total reflection of X-rays. *Phys. Rev.*, 1954, **95**(2), 359–369.
14. James, R. W., *The Optical Principles of the Diffraction of X-rays*. Bell, London, 1965.
15. Henke, B. L., Gullikson, E. M. and Davis, J. C., X-ray interactions: photoabsorption, scattering, transmission and reflection at $E = 50$–30000 eV, $Z = 1$–92. *Atom. Data Nucl. Data*, 1993, **54**(2), 181–342.
16. Masson, O., Guinebretière, R. and Dauger, A., Reflection asymmetric powder diffraction with flat-plate sample using a curve position-sensitive detector (INEL CPS 120). *J. Appl. Cryst.*, 1996, **29**, 540–546.
17. Kiessig, H., *Ann. Phys. (Leipzig)*, 1931, **10**, 769–788.
18. Rizzato, A. P., Santilli, C. V. and Pulcinelli, S. H., X-ray reflectivity of zirconia based sol–gel coatings on borosilicate glasses. *J. Non-Cryst. Solids*, 1999, **247**, 158–163.
19. Lenormand, P., Lecomte, A., Dauger, A., Mary, C. and Guinebretière, R., Réflectometrie et diffusion centrale de rayons X sur couches minces élaborées par voie sol gel. *J. Phys. IV France*, 2000, **10**, 255–264.
20. Hodgson, S. N. B. and Weng, L., Sol–gel processing of tellurium oxide and suboxide thin films with potential for optical data storage application. *J. Sol Gel Sci. Technol.*, 2000, **18**, 145–158.
21. Cain, M. G. and Lange, F. F., Heteroepitaxy of cubic zirconia on basal and prismatic planes of sapphire. *J. Mater. Res.*, 1994, **9**(3), 674–687.
22. Boulle, A., Masson, O., Guinebretière, R. and Dauger, A., X-ray diffraction from epitaxial oxide layers grown from sol gel. *Thin Solid Films*, 2003, **434**, 1–6.
23. Holy, V., Kubena, J., Ohlidal, I., Lischka, K. and Plotz, W., X-ray reflection from rough layered systems. *Phys. Rev. B*, 1993, **47**(23), 15896–15903.
24. Jergel, M., Holy, V., Majkova, E., Luby, S. and Senderak, R., Interface evolution in a W/Si multilayer after rapid thermal annealing studied by X-ray reflectivity and diffuse scattering. *J. Appl. Cryst.*, 1997, **30**, 642–646.