Sol−Gel Synthesis of β-Al_2TiO_5 Thin Films at Low Temperature

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β-Al_2TiO_5 thin films were obtained by dip-coating silicon substrates in acid-catalyzed precursor sols of aluminum and titanium alkoxides with and without acetyl acetone as a chelating agent and subsequent firing at 700 °C. Nuclear magnetic resonance and mass spectra of the precursor sols demonstrated that synthesis without a chelating agent leads to the most extensive polymerization. X-ray photoelectron spectroscopy depth profiles showed that the composition of the films was homogeneous throughout their thicknesses. The crystallization of the films was studied as a function of the firing time and temperature. The films were amorphous up to 600 °C and crystalline β-Al_2TiO_5 was formed at 700 °C. From 800 up to 1200 °C, titania (anatase and rutile) phases were also detected, without decomposition of the metastable β-Al_2TiO_5 phase. The films fabricated from the sols without chelating agents showed a lower tendency to decompose into the thermodynamically stable phases rutile titania and α-Al_2O_3. The formation of β-Al_2TiO_5 at low temperatures is attributed to a diffusion-limited crystallization process, which takes place in the conditions of high homogeneity at the molecular level reached in the sol−gel synthesis as shown by spectroscopic analysis.

Introduction

Aluminum titanate is a ceramic material characterized by low average thermal expansion, good thermal shock resistance, and low thermal conductivity. Because of its peculiar characteristics, it has been the subject of several investigations aimed toward mechanical and catalytic applications.[1−4] In particular, the preparation of thin films is expected to have very appealing potential applications, such as high-temperature protective coatings.[5−7]

Aluminum titanate is conventionally formed by a solid-state reaction between crystalline rutile TiO_2 and α-Al_2O_3 at temperatures higher than the eutectoid temperature (1280 °C).[1] It is known to exist in two allotropic forms, α and β. The low-temperature phase, β-Al_2TiO_5, has two temperature ranges of stability, the first from room temperature up to around 750 °C, and the second from 1280 °C up to the inversion temperature at 1820 °C.[1] The high-temperature phase, α-Al_2TiO_5, is stable from 1820 °C up to its melting temperature, 1860 °C.[1] Below 1280 °C, aluminum titanate has the tendency to decompose, into α-Al_2O_3 and rutile titania.[8] The decomposition process is very slow below 900 °C, while in the range 900−1200 °C it becomes faster with a maximum decomposition rate at 1100−1150 °C, a range in which full decomposition is observed after annealing from 5 to 50 h.[9−11]

Sol−gel processing has been extensively studied as an alternative route to preparing aluminum titanate[12−22]

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because it gives the possibility of controlling the composition at the molecular level to obtain a very homogeneous material. However, in most of the cases the syntheses were aimed at obtaining ultrafine powders of alumina and titania as precursor materials for β-Al_2TiO_5 prepared by solid-state reaction at high temperature.[12−17,21,22]

Recently, it was found that sol−gel processing allows one to obtain β-Al_2TiO_5 powders directly from the amorphous phase[18−20] at temperatures much lower than the eutectoid one. This effect was observed by using either a nonhydrolytic synthetic route[19,20] or the hydrolysis of a sol of aluminum and titanium alkoxides with chelating agents.[18] In both cases the authors have assumed that the high homogeneity reached at the molecular level in the precursor sols led to the formation of a metastable β-Al_2TiO_5 crystalline phase directly from the amorphous phase. This direct crystallization of aluminum titanate was observed at $T > 600$ °C for the powders prepared by the nonhydrolytic route[19,20] and around 800 °C for those synthesized by the alkoxide hydrolysis.[18] However, the metastable β-Al_2TiO_5 phase obtained by Bonhomme-Coury et al.,[18] via alkoxide hydrolysis, quickly decomposed at temperatures higher than 800 °C into rutile TiO_2 and α-Al_2O_3. After decomposition the two phases reacted again at 1360 °C to give β-Al_2TiO_5. The low-temperature β-Al_2TiO_5 phase prepared in this way showed, therefore, a limited thermal stability.[18] On the contrary, β-Al_2TiO_5 powders prepared by the nonhydrolytic route did not decompose below 1180 °C and phase separation during prolonged thermal annealing at 1150 °C was not completed after 70 h.[19,20] This synthesis, however, is not suitable for the fabrication of coating films.

Given that the use of aluminum titanate films might lead to important technological applications, as stated above, the synthesis of thin films at temperatures as low as possible is extremely interesting. The processing method should not be expensive and the prepared aluminum titanate coatings should have an extended range of thermal stability.

Few examples of β-Al_2TiO_5 film synthesis have been reported in the relevant literature. β-Al_2TiO_5 protective coatings were fabricated by sol−gel processing on SiC and Si_3N_4 ceramics.[6] The films were prepared from acid-catalyzed sols of aluminum tri-*sec*-butoxide and titanium butoxide, without any chelating agent, after thermal treatments at 1300 °C for 10 h. This route, however, is convenient only for this very specific application because the high temperature necessary to obtain β-Al_2TiO_5 requires the use of suitable substrates. $Al_xTi_yO_z$ thin films were prepared by ion-beam-induced chemical vapor deposition.[7] Films with the composition Al_2TiO_5 were obtained by controlling the Al/Ti ratio. At around 750 °C, however, the aluminum titanate easily dissociated.

We report here two different sol−gel synthetic routes leading to the formation of β-Al_2TiO_5 thin films at temperatures lower than the eutectoid one, with thermal stability extended in a wide range of temperatures. The progress of the hydrolysis and condensation reactions has been monitored by spectroscopic analysis of the sols (nuclear magnetic resonance and mass spectrometry). The structural evolution of the materials has been studied as a function of the annealing temperature.

Experimental Section

Materials. Aluminum tri-*sec*-butoxide (Al(O-*s*-Bu)$_3$), titanium tetrabutoxide (Ti(OBu)$_4$), and 2,4-pentanedione (acac) (Aldrich) were reagent grade and were used without further purification. Nitric acid (Prolabo), 1 N, and absolute ethanol (Carlo Erba) were used as received.

Sol Preparation. All the preparations were carried out under N_2.

Sol AlTi1. A sol (S1) was prepared by adding Al(O-*s*-Bu)$_3$ (1.6 mL, 6.3 mmol) to a solution of acac (0.65 mL, 6.3 mmol) in EtOH (22 mL). The solution was refluxed under magnetic stirring for 1 h.

A second sol (S2) was prepared adding Ti(OBu)$_4$ (1.1 mL, 3.2 mmol) to a solution of acac (0.16 mL, 1.6 mmol) in EtOH (3 mL). The solution was stirred at room temperature for 10 min.

S1 and S2 were then mixed and HNO_3 (1 N) (0.06 mL) was added. The resulting sol was stirred at room temperature for 30 min.

Sol AlTi2. Al(O-*s*-Bu)$_3$ (1.6 mL, 6.3 mmol) was carefully added to refluxing EtOH (50 mL). Ti(OBu)$_4$ (1.1 mL, 3.2 mmol) was slowly added under magnetic stirring. The solution was cooled to room temperature, and then HNO_3 (1 N) (0.06 mL) was added. The resulting solution was stirred for 1 h.

Materials Preparation. Films were deposited from fresh sols by dip-coating in a humidity-controlled box, with a relative humidity lower than 30%. Silicon wafers were used as substrates. The withdrawal speed was 250 and 100 cm min^{-1} for Sol AlTi1 and Sol AlTi2, respectively. The samples were put directly in the preheated furnace after the deposition and fired in air at the temperatures of 600, 700, 800, 1000, 1150, and 1200 °C for different treatment times. The coating thickness was measured with a profilometer. Thicknesses of about 100−200 nm per single layer were obtained.

Powders were obtained from solutions poured into Petri dishes and maintained in a thermostatic chamber for 1 day at 60 °C.

Characterization. *Nuclear Magnetic Resonance and Mass Spectrometry.* Fractions for nuclear magnetic resonance (NMR) and mass spectrometry (MS) were evaporated in a vacuum at 40 °C, obtaining solid residues that were used as such for MS, or dissolved in CD_2Cl_2:CH_2Cl_2 = 1:2 for NMR measurements.

^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 100.56 MHz. Chemical shifts are given in ppm from tetramethylsilane (TMS) and are referenced against solvent signals.

Direct inlet mass spectra (electronic impact EI, 70 eV; source temperature, 200 °C; final probe temperature, 400 °C) were recorded on a VG Quattro spectrometer.

XPS Analysis. The surface and bulk chemical composition of the films was investigated by X-ray photoelectron spectroscopy (XPS) using a Perkin-Elmer Φ 5600-ci spectrometer with nonmonochromated Mg Kα radiation (1253.6 eV). The working pressure was smaller than 5×10^{-8} Pa. The spectrometer was

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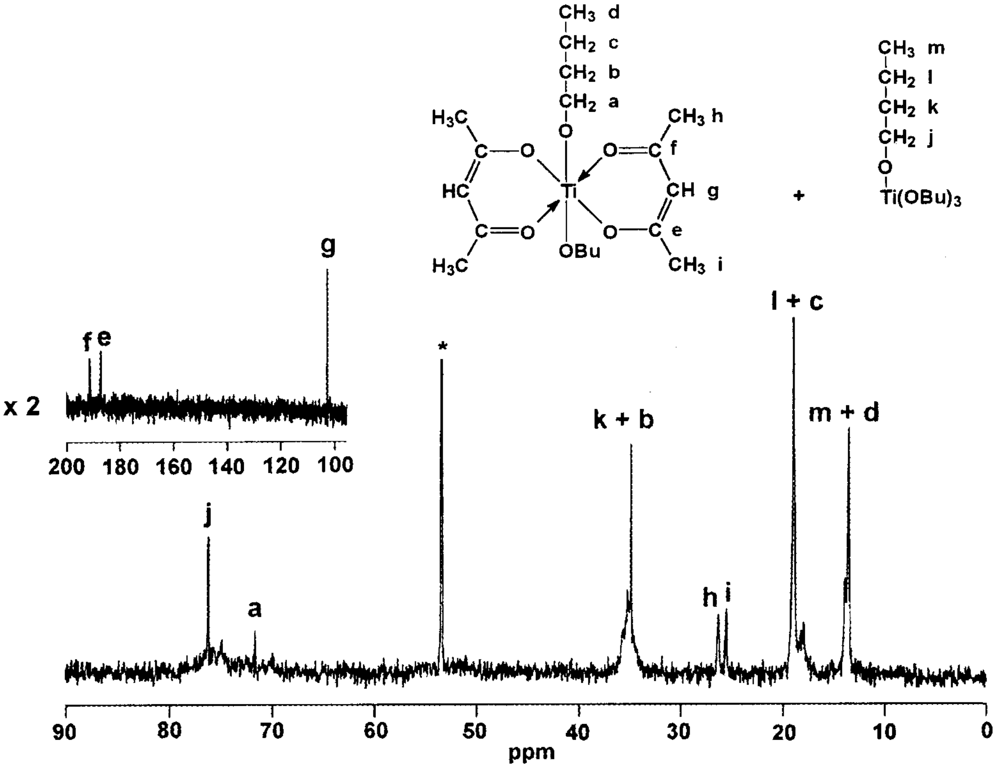

Figure 1. ^{13}C NMR spectrum in CD_2Cl_2:CH_2Cl_2 1:2 of sol S2. An asterisk marks the solvent signal.

calibrated by assuming the binding energy (BE) of the Au $4f_{7/2}$ line at 83.9 eV with respect to the Fermi level. The standard deviation for the BE values was 0.15 eV. Survey scans were obtained in the 0–1150 eV range. Detailed scans were recorded for the Al 2p, Ti 2p, O 1s, C 1s, and Si 2p regions. The chemical composition across the films was evaluated by in-depth analysis. Depth profiles were obtained by Ar^+ sputtering at 2.5 keV with an argon partial pressure of 5×10^{-6} Pa. The analysis involved Shirley-type background subtraction,[23] nonlinear least-squares curve fitting, adoption of Gaussian–Lorentzian peak shapes, and peak area determination by integration. The atomic compositions were then evaluated using sensitivity factors supplied by Perkin-Elmer, taking into account the geometric configuration of the apparatus. The samples were introduced directly, by a fast entry lock system, into the XPS analytical chamber.

X-ray Diffraction. X-ray diffraction analysis (XRD) was performed on the films using a diffractometer with a glancing angle configuration for thin film samples. CuKα, operating at 40 kV and 50 mA, was used as the radiation source (1 scan, 5-s acquisition time, $2\theta°$ angle from 15° to 70° and a fixed glancing angle $\theta = 0.5°$). The average crystallite size was calculated from the Scherrer equation after the experimental patterns were fitted using the method described by Enzo et al.[24]

Results and Discussion

NMR and MS Analysis. Sol precursors of β-Al_2TiO_5 were prepared by reacting under acidic conditions the two metal alkoxides as such (sol AlTi2) or in the presence of acetylacetone (acac) as a chelating agent (sol AlTi1).

Differences observed in the materials prepared under different conditions are related to the characteristics of the polymers generated by hydrolysis and condensation reactions of the reactants. Direct analysis of the sol may help understanding such reactions and identifying the most efficient synthetic strategy. NMR is an ideal tool for such a purpose. We have chosen to study the ^{13}C spectra of the sols because the large chemical shift range allows easy identification of the different species in solution.

The addition of acac (in substoichiometric ratio) to an ethanolic solution of $Ti(OBu)_4$ generates the formation of $Ti(OBu)_2(acac)_2$ identified by the resonances of the quaternary carbon atoms bound to the chelating oxygen atoms ($\delta = 196, 188$) and by the resonances of the olefinic (=CH) carbon at 101 ppm (Figure 1). No evidence for ligand exchange due to the solvent has been observed.[25]

Al(O-*s*-Bu)$_3$ also reacts in EtOH with acac to give $Al(acac)_3$, $Al(OEt)_3$, and 2-BuOH (Figure 2). Substitution of *s*-butoxy by ethoxy groups seems to be complete as indicated by the very small line width of the resonances due to 2-butanol. Some condensation of $Al(OEt)_3$ seems also to have occurred by the multiplicity of the resonances observed (broadened by Al quadrupole moment) that indicate the existence of different coordination environments.

Mixing of the two sols (S1 and S2, see the Experimental Section) and addition of nitric acid generates sol AlTi1 whose ^{13}C NMR spectrum is shown in Figure 3. The broadness of the resonances indicates an extensive degree of polymerization. No dissociation of acac occurred during the formation of the sol as shown by the lack of the resonance due to C=O of free acac at 202.9 ppm. Acetylacetone is then coordinated to the two metals in the polymer in different coordination environ-

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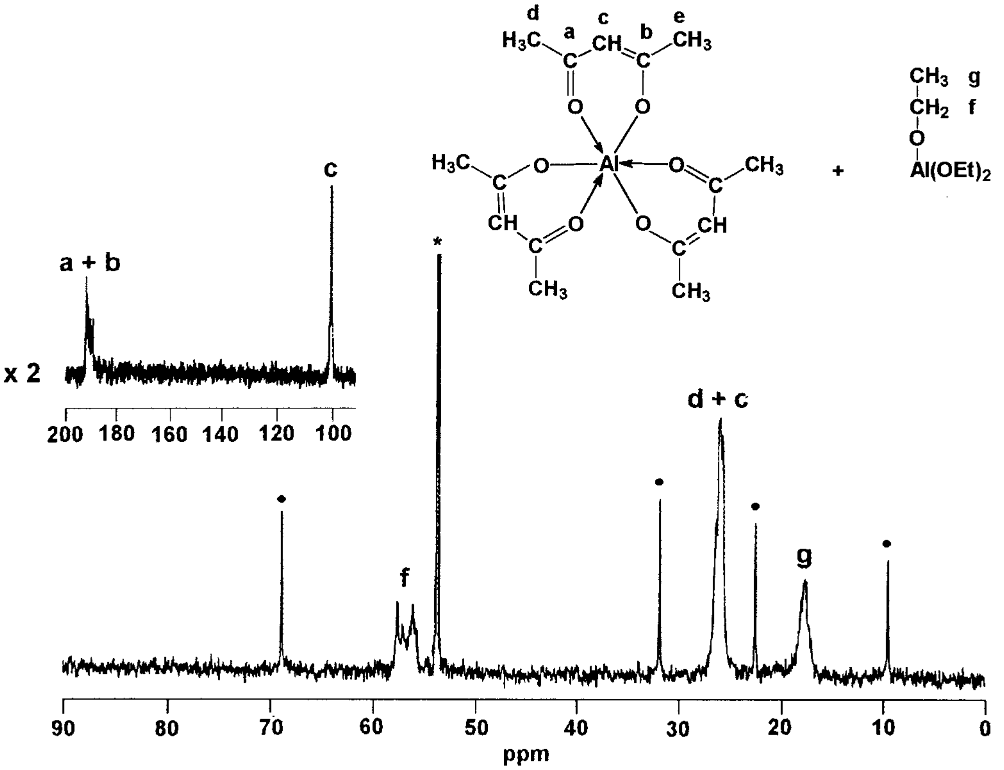

Figure 2. ^{13}C NMR spectrum in CD_2Cl_2:CH_2Cl_2 1:2 of sol S1. Resonances due to 2-butanol are labeled with a filled dot. An asterisk marks the solvent signal.

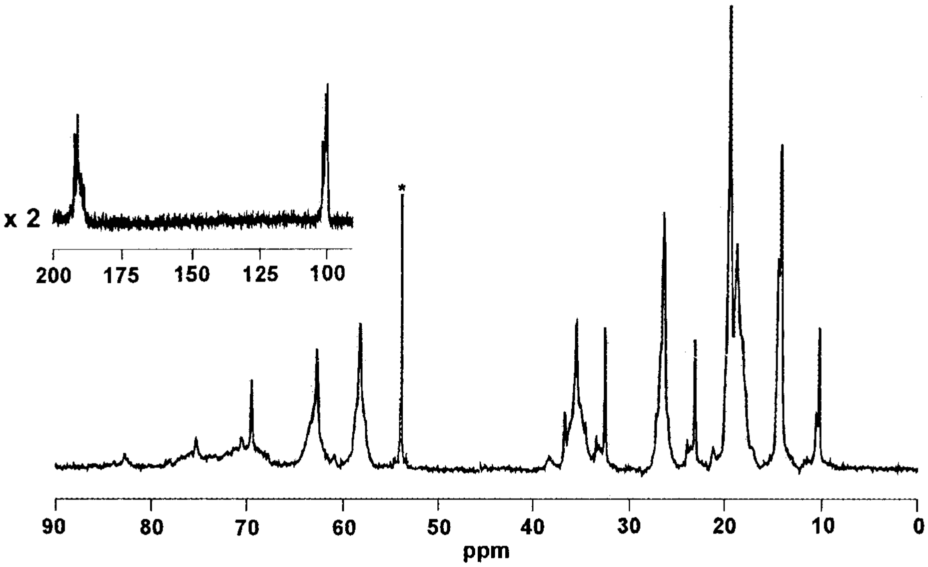

Figure 3. ^{13}C NMR spectrum in CD_2Cl_2:CH_2Cl_2 1:2 of sol AlTi1. An asterisk marks the solvent signal.

ments as shown by the several resonances observed for the carbonyl groups between 186 and 194 ppm.

To investigate the structure of sol AlTi2, prepared without acac, the ^{13}C NMR spectra of Al(O-*s*-Bu)$_3$ and Ti(OBu)$_4$, dissolved in EtOH, then dried, and redissolved in dichloromethane, were examined. While Ti(OBu)$_4$ is unaffected by such a procedure, a complete ligand exchange reaction has been evidenced in the case of Al(O-*s*-Bu)$_3$ which reacts to give 2-BuOH and Al(OEt)$_3$, as shown by the presence of two resonances (58.5 and 18.3 ppm).

The ^{13}C NMR spectrum of the AlTi2 sol (Figure 4) showed mainly the sharp resonances of the free alcohols (EtOH, 1-BuOH, and 2-BuOH) derived from hydrolysis and condensation reactions, superimposed to some weak broad resonances (δ 18−20, 34−36, and 56−58 ppm) that can be attributed to residual metal-bound alkoxide chains. The low intensity and broadness of such resonances is indicative of a very high degree of polymerization.

Mass spectrometry is widely used in chemistry to easily obtain structural information. The molecular peak cannot be observed in electronic impact mass spectra of high molecular weight polymers but analysis of the fragmentation pattern can still give important information on the structure examined. We have then measured the EI mass spectra of the solids obtained by rotary evaporating the different sols. The spectrum of AlTi2

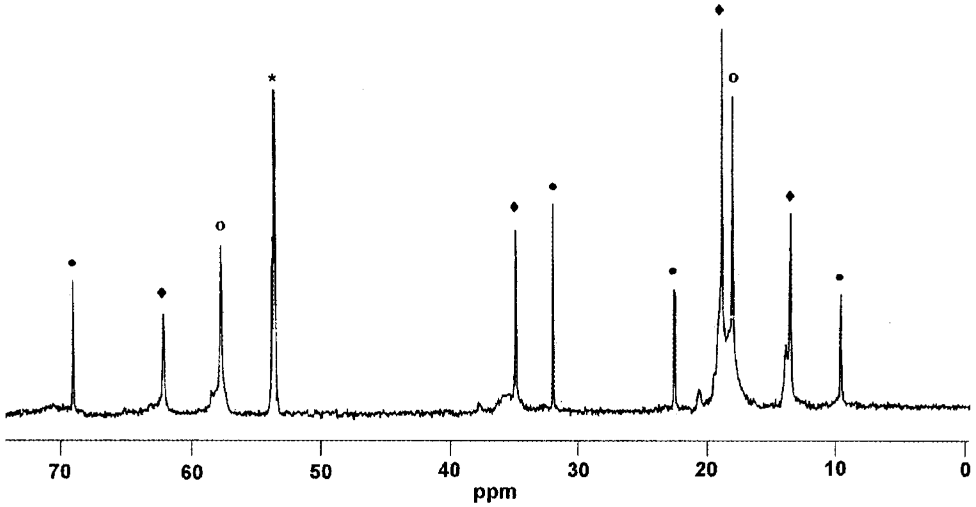

Figure 4. ^{13}C NMR spectrum of sol AlTi2 in CD_2Cl_2:CH_2Cl_2 1:2. An asterisk marks the solvent signal. Resonances due to different alcohol are labeled: (○) ethanol, (◆) butanol, (●)2-butanol.

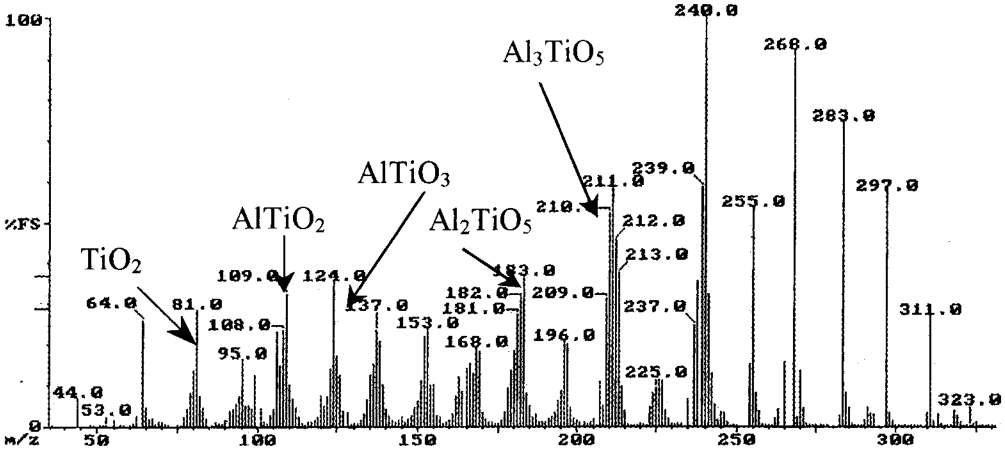

Figure 5. EI mass spectrum of AlTi1.

(Figure 5) clearly shows the fragmentation of an Al−Ti. Namely, peaks attributable to $AlTiO_2^+$, $Al_2TiO_5^+$, $Al_3TiO_5^+$, and so on can be observed in the spectrum. All titanium-containing peaks showed the isotopic pattern typical of the element. Also, peaks that revealed the presence of metal-bound alkoxides were present in the spectrum. A peak at $[M + 1]^+ = 81$ m/z was attributed to TiO_2^+.

The spectrum has been compared with those of sol−gel-derived pure TiO_2 and Al_2O_3. The most relevant peaks of the titania mass spectrum were observed at 81 and 162 m/z corresponding to monomeric and dimeric titania. The molecular peak, Al_2O_3, was also observed in the spectrum of alumina.

To verify that the peak due to Al_2TiO_5 was not generated by a recombination reaction in the spectrometer, the spectrum of a 1:1 mechanical mixture of Al_2O_3 and TiO_2 was recorded. Such a spectrum resulted in being simply the sum of those of the two oxides and did not contain the pattern present in the spectrum of AlTi2.

The AlTi1 sample gives a fragmentation pattern very similar to that of AlTi2. Peaks due to the presence of acac were also observed. In this spectrum, however, peaks due to the alkoxide precursors and to the metal acetylacetonato complexes were also present, indicating a noncompleted condensation.

An evaluation of the Al_2TiO_5/TiO_2 ratios in the materials obtained from the different preparations can be calculated by the intensity ratios of the corresponding peaks in the mass spectra. The ratio was 0.66 and 1.33 for the samples AlTi1 and AlTi2, respectively, confirming that the most efficient synthesis is the one without chelating agents, as derived from NMR.

XPS Analysis. An XPS investigation was preliminarily performed on mono-component TiO_2 and Al_2O_3 films used as a reference. The layers were deposited on silicon wafers from ethanolic solutions of the individual alkoxide precursors, both without and with acetylacetone. The samples were treated at $T \geq 60$ °C. BEs and peak features were determined for Ti 2p, Al 2p, and O 1s XPS lines. After correction for sample charging, the BE values [TiO_2:(Ti $2p_{3/2}$) = 458.8 eV; O 1s = 529.9 eV; Al_2O_3:(Al 2p) = 73.9 eV; O 1s = 531.3 eV] were found to be in agreement with the values reported in the literature.[26] The BE values for the Al 2p, Ti 2p, O 1s, and C 1s lines as well as the elemental atomic percentages were then analyzed for the films prepared from both AlTi1 and AlTi2 sols as a function of the annealing conditions. As a general remark about film purity and

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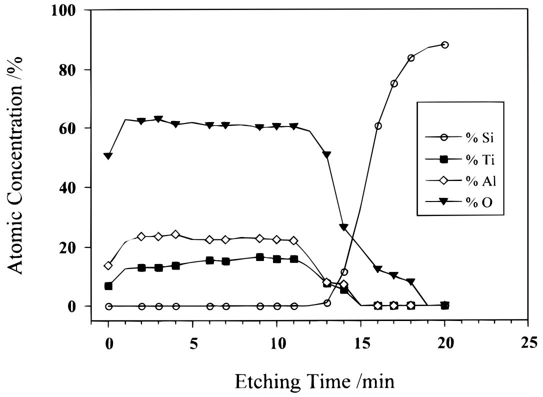

Figure 6. XPS depth profile for the AlTi2 film heat-treated at 700 °C. The in-depth distributions of aluminum, titanium, oxygen, and silicon are reported.

Table 1. Evaluation of the Oxygen Auger Parameter α [BE(O 1s) + KE(OLL)] in the AlTi2 Films

	BE (eV)			α^a (eV)
sample	Al 2p	Ti 2p	O 1s	O
TiO_2		458.8	529.9	1041.9
Al_2O_3	73.9		531.3	1038.6
Al_2TiO_5 (ref 7)	73.5	458.5	530.3	1040.2
AlTi60	73.8	458.5	529.9−531.4	1041.4−1039.6
AlTi700	73.9	458.7	530.6	1040.6

[a] The α values in TiO_2 and Al_2O_3 are reported as references.

in-depth distribution of the various species, XPS profiles showed that the hydrocarbon content of the coatings decreased with increasing firing temperature.

Figure 6 shows the quantitative profile of the XPS Al 2p, Ti 2p, Si 2p, and O 1s peaks at different depths for the AlTi2 film fired at 700 °C. At 700 °C, adventitious carbon was detected only as a surface contaminant. Al 2p and Ti 2p regions showed a uniform distribution along the film thickness, with a constant composition, so that a common chemical origin for Al^{3+} and Ti^{4+} species can be hypothesized.

The BE values of the Ti $2p_{3/2}$, Al 2p, and O 1s XPS peaks measured for the various samples tested are reported in Table 1, together with the oxygen Auger parameter (α) values and the literature data[7] for Al_2O_3, TiO_2, and β-Al_2TiO_5. Their analysis showed that the BEs of the Ti $2p_{3/2}$ and Al 2p peaks were in the range typical for Ti^{4+} and Al^{3+} ions surrounded by oxygen atoms. No significant differences were observed among the various samples. This implies that a straightforward indication of titanate formation cannot be derived merely considering the binding energies of the two metals.

Therefore, an analysis of the O 1s photoelectronic peaks was carried out. All the samples showed for the O 1s XPS peak a complex band shape, which was deconvoluted adopting Gaussian−Lorentzian peak shapes. At low annealing temperatures the O 1s lines showed a significant broadening (fwhm ≈ 3.5 eV), thus suggesting the coexistence of different chemical environments. The peak deconvolution of the O 1s regions demonstrated that the peak was split at least into two bands centered around 529.9 and 531.4 eV (Figure 7). These components might represent limited environments associated with Ti−O−Ti and Al−O−Al bonds, respectively, although other hypotheses cannot be excluded, such as the presence in the films of hydroxylated +Ti−OH or =Al−OH species, or even mixed Al−O−Ti bonds. The higher the annealing temperature, the more symmetric and sharper the O1s lines. Moreover, the BEs of the two oxygen-related components shift to the common value centered at 530.6 eV (Figure 7). This BE value as well as the peak features suggested the presence of a single-oxygen site, around which the average composition of both Ti and Al atoms might be able to modulate the potential.

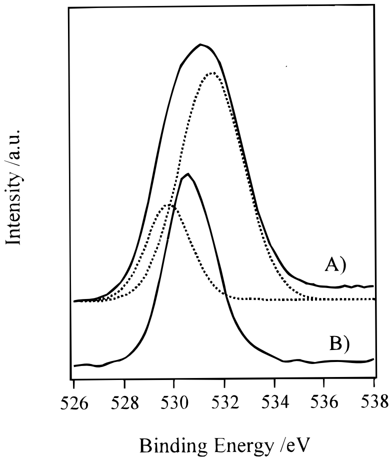

Figure 7. XPS O 1s regions for samples AlTi2 heat-treated at 60 °C (A) and 700 °C (B). Peak deconvolution is also shown and the two components centered at 529.9 and 531.4 eV are represented with dotted lines.

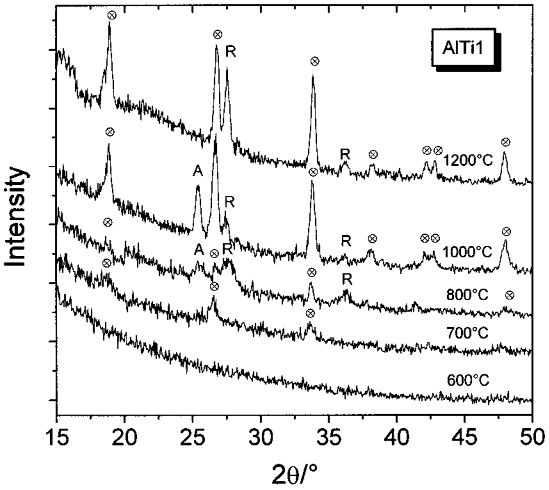

Figure 8. XRD patterns of AlTi1 films deposited on silicon and fired 1 h at 600, 700, 800, 1000, and 1200 °C. R = titania rutile; A = titania anatase; ⊗ = aluminum titanate.

This hypothesis was strengthened by the evaluation of the oxygen Auger parameter[7] α [BE(O 1s) + KE(OKLL)], reported in Table 1. One can observe that the oxygen α for the films annealed at 60 °C were closer to the values measured for Al_2O_3 and TiO_2, while the oxygen α for the films annealed at 700 °C was very similar to the α of β-Al_2TiO_5, suggesting thus that the local arrangement of the atoms must be very similar in the two cases.

Crystallization and Thermal Stability. The formation of the different phases as a function of annealing times and temperature was followed by XRD. Figure 8 shows the XRD patterns of AlTi1 films deposited on silicon and fired for 1 h at different temperatures. At

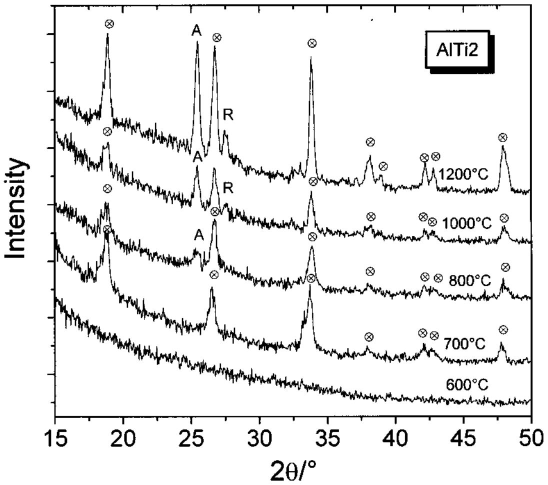

Figure 9. XRD patterns of AlTi2 films deposited on silicon and fired 1 h at 600, 700, 800, 1000, and 1200 °C. R = titania rutile; A = titania anatase; ⊗ = aluminum titanate.

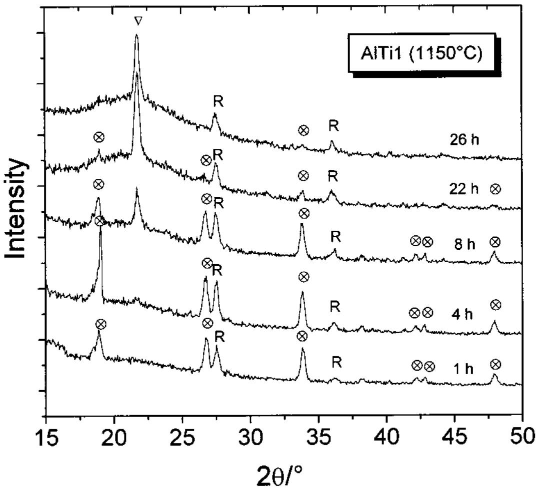

Figure 10. XRD patterns of AlTi1 films deposited on silicon and fired for different times at 1150 °C. R = titania rutile; ⊗ = aluminum titanate.

600 °C the films were amorphous. At 700 °C, the peaks at 18.8°, 26.5°, and 33.7° in 2θ of β-Al_2TiO_5 were observed, corresponding to the (020), (110), and (023) reflections (JCPDS card no. 26-40). At 800 °C additional peaks attributed to TiO_2 in the anatase structure (JCPDS card no. 21-1272), at 25.3° (101), and TiO_2 in the rutile structure (JCPDS card no. 21-1276), at 27.5° (110) and 36.1° (101), were detected. A strong increase in the intensity of the β-Al_2TiO_5 peaks was observed in the XRD patterns of the films fired at 1000 °C; the anatase TiO_2 peak also increased its intensity. At 1200 °C, the anatase TiO_2 peak was no longer observed, while the rutile TiO_2 peaks increased their intensity. This was attributed to the transformation of anatase TiO_2 to rutile TiO_2, and further crystallization of the rutile TiO_2 phase directly from the amorphous phase. Given that the α-Al_2O_3 peaks, which should also appear from the decomposition of aluminum titanate, were not observed and that the intensity of β-Al_2TiO_5 peaks increased with raising the firing temperature, the hypothesis of the formation of rutile TiO_2 from the decomposition of β-Al_2TiO_5 was discarded.

Figure 9 shows the XRD patterns of AlTi2 films fired for 1 h at different temperatures. At 600 °C the films were amorphous. At 700 °C the peaks at 18.8° (020), 26.5° (110), 33.7° (023), the overlapped 38° (130) and 38.1° (040), 42.1° (024) and 42.6° (132), and the overlapped 47.7° (133) and 47.8° (043) in 2θ of the β-Al_2TiO_5 phase were observed. At 800 °C only a weak peak due to TiO_2 in the anatase structure, at 25.3° (101), was observed, while differently from AlTi1 no crystallization of rutile was yet found. At 1000 °C the anatase peak increased in intensity and a weak peak due to TiO_2 rutile, at 27.5° (110), was observed. At 1200 °C a strong increase in intensity of the TiO_2 anatase and β-Al_2TiO_5 peaks was detected, together with a little increase of the TiO_2 rutile peak. Crystallization of α-Al_2O_3 was not observed in either of these films.

The crystallization behavior during firing of AlTi1 and AlTi2 films (Figures 8 and 9) showed the larger intensity of the β-Al_2TiO_5 peaks in AlTi2 than in AlTi1. This finding, in agreement with the results of MS analysis, is an indication that the films prepared from the AlTi2 sols have a larger tendency to crystallize in the metastable form at low temperature. Moreover, the presence of anatase titania in AlTi2 films was observed, even at higher firing temperatures, where one would expect the anatase to rutile titania transformation to occur.

Few examples of this kind of crystallization leading to metastable compounds have been reported in the sol−gel literature.[18−20,27,28] This crystallization takes place in conditions of limited diffusion and is related to a high structural homogeneity at the molecular scale.[27] At low temperatures, where long-range diffusion is limited, a binary oxide can crystallize by short-range ordering, if the homogeneity is large enough.[27,28] The difference in the structure between AlTi1 and AlTi2 is also reflected in the inhibition of the anatase to rutile transformation in AlTi2 (Figure 9). It is, however, difficult to state without other specific investigations if this difference plays any role in the formation and stabilization of β-Al_2TiO_5.

To study the thermal stability of the films, XRD analysis was performed on films fired at 1150 °C, the most critical temperature for β-Al_2TiO_5 decomposition,[10,11] as a function of time. In the AlTi1 films (Figure 10), the aluminum titanate phase was present together with rutile titania and up to 8 h of annealing no significant changes were observed. After 22 h, only weak β-Al_2TiO_5 peaks were detected, while after 26 h only rutile titania was found. After 8 h of firing an intense peak, at 22° (101) in 2θ, due to crystallization of cristobalite from the oxidation of the silicon substrate, was also observed. In the AlTi2 films (Figure 11), titania in the rutile and anatase structures was observed together with β-Al_2TiO_5; cristobalite was also detected for the films fired more than 22 h. In this range of annealing times, up to 30 h, only a very weak decrease in intensity of the β-Al_2TiO_5 peaks was observed.

The changes with time of the areas of the β-Al_2TiO_5 peak at 33.7° during the annealing at 1150 °C are shown in Figure 12. AlTi1 showed an abrupt decrease after 8 h of firing, while AlTi2 had, up to 30 h of firing, a decrease of only about 25%.

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(28) Barboux, P.; Griesmar, P.; Ribot, F.; Mazerolles, L. *J. Solid State Chem.* **1995**, *117*, 343.

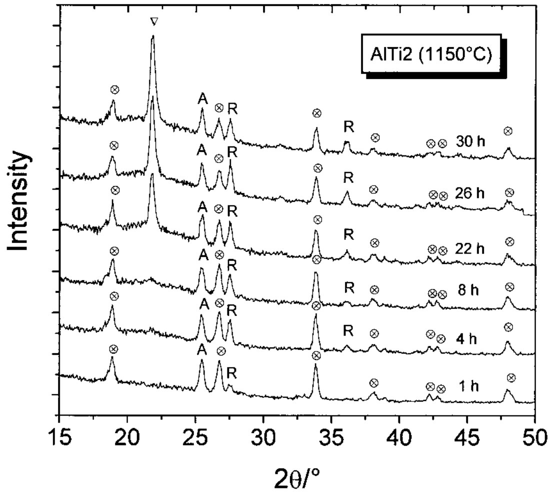

Figure 11. XRD patterns of AlTi2 films deposited on silicon and fired for different times at 1150 °C. R = titania rutile; A = titania anatase; ⊗ = aluminum titanate.

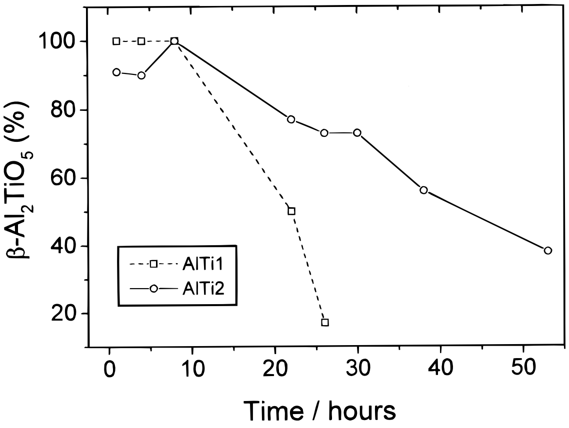

Figure 12. Variations of the area of the β-Al_2TiO_5 peak at 33.7°, as a function of annealing time at 1150 °C. The lines are visual aids only.

The variation of the β-Al_2TiO_5 crystallite dimensions during the annealing at 1150 °C is reported in Figure 13. The trend is similar to that observed for the areas in Figure 12; the peak (023) at 33.7° was used for the calculations. A full quantitative evaluation was, however, difficult to achieve because of the reaction during the annealing process of the silicon oxide from the substrate.

The XRD data showed that, in AlTi2 films, where a high homogeneity at the molecular scale is reached, metastable β-Al_2TiO_5 is formed directly from the amorphous phase at 700 °C and has a better thermal stability compared to AlTi1 and with literature data.[18] This transformation is, however, not completed and a residual amorphous phase, which crystallizes to the titania phases at higher firing temperatures, is present. We can suppose that the presence of the titania crystallites and amorphous alumina can stabilize the aluminum titanate phase by limiting the growth of β-Al_2TiO_5 within the critical size.

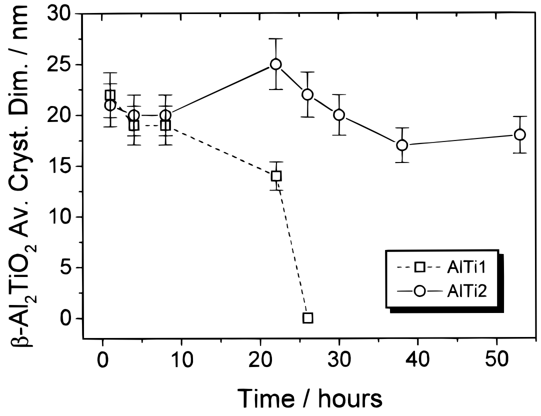

Figure 13. Variations of the β-Al_2TiO_5 dimensions calculated from the diffraction peak at 33.7°, at different firing temperatures. The lines are visual aids only.

Conclusions

Acid-catalyzed solutions of titanium and aluminum alkoxides have been used to synthesize β-Al_2TiO_5 films at low temperature. A metastable β-Al_2TiO_5 phase crystallizes in the films at around 700 °C directly from the amorphous phase. At higher annealing temperatures TiO_2 rutile and anatase are also detected but β-Al_2TiO_5 does not decompose, up to 1200 °C. The films synthesized without using chelating agents in the precursor sol show a longer thermal stability. It was thus possible to obtain a metastable compound such as β-Al_2TiO_5 by sol−gel processing exploiting the high homogeneity obtained already in the sols.

The study of the precursor sols using chemical tools such as NMR and MS is very effective in assessing the properties of the materials. In fact, the better reactivity observed for the sol prepared without chelating agents is reflected in the preparation of more stable β-Al_2TiO_5 thin films.

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