Constitution and crystallization behaviour of ultrathin physical vapor deposited (PVD) Al_2O_3/SiO_2 laminates

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Abstract

Ultrathin Al_2O_3/SiO_2 multilayers were produced by physical vapor deposition (PVD) using a double source jumping beam PVD-coater. Al_2O_3/SiO_2 multilayer formation is controlled by the electron beam jumping frequency yielding double-layer thicknesses of about 2, 5, 9, and 30 nm. The as-deposited Al_2O_3/SiO_2 laminates are non-crystalline and display periodical contrast modulations in TEM cross-sections as long as the nominal thickness of the Al_2O_3/SiO_2 double-layer is > 5 nm. EDX line scans and ^{29}Si–MAS–NMR spectroscopy provide evidence of nanosized pure SiO_2 and pure Al_2O_3 layers. XRD analyses show that films consisting of 30 nm thick Al_2O_3 and SiO_2 layers at 1000°C form transition alumina only. Transition alumina plus minor amounts of mullite appear at 1000°C in alumino silicate coatings with intermediate Al_2O_3 and SiO_2 layer thickness (5 and 9 nm), while only mullite occurs in samples with 2 nm thick compositional modulations. The crystallization of PVD-produced alumino silicate films with double layer thicknesses > 5 nm behaves similar to diphasic (type II) mullite precursors, while Al_2O_3/SiO_2 double-layers 2 nm thick behave like single phase mullite precursors (type I). The latter is surprising because of the diphasic character of the double layers. Obviously, two conditions are required for mullite formation at 1000°C: Interdiffusion-produced chemical homogeneization between Al_2O_3 and SiO_2 layers, and formation of homogeneization zones large enough for mullite nucleation (about 2 to 5 nm in size). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3–SiO_2; Mullite

1. Introduction

Electron beam physical vapor deposition (EB–PVD) is a state-of-the-art technique to produce thermal barrier coatings (TBC) for highly stressed turbine blades and vanes in aero-engines and stationary gas turbines.[1] Simple compounds or elements can be deposited using single source evaporation. In case of compounds with two or more chemical constituents, however, evaporation from at least two sources is required, especially if the vapor pressure differs strongly. Double source coaters are equipped either with two electron guns or are designed as single electron beam installation using a jumping beam technology. Recent developments in jumping beam PVD are summarized by Schulz et al.[2]

Mullite is a widely used ceramic material for structural and functional applications.[3] Only little information exists, however, on vapor deposition of mullite or alumino silicates, respectively. CVD mullite deposition was carried out succesfully using the $AlCl_3$–$SiCl_4$–CO_2–H_2 system.[4–6] The process takes place above 1000°C, resulting in crystalline mullite coatings. Reactive sputtering, on the other hand, using Al and Si targets and low oxygen pressures (3.6×10^{-3} mbar) yields non-crystalline alumino silicate film that transforms into mullite after heating at 1000°C.[7] No data about EB–PVD of alumino silicates were published so far, though our own preliminary investigations indicated that alumino silicate films formed by EB–PVD are also non-crystalline. Non-crystalline alumino silicates are of interest from scientific and technological points of view since they are used as starting materials for high performance mullite ceramics.

Different types of mullite precursors were described in literature, depending on the degree of cation mixing in the non-crystalline mullite precursor powders. Cation mixing of single phase (type I) mullite precursors appears homogeneous on atomic scale based on ^{29}Si MAS NMR experiments. These precursors transform into (Al_2O_3-rich) mullite at ca. 980°C[8] in the same way as rapidly quenched aluminosilicate glasses.[9] Diphasic mullite precursors (type II), on the other hand, consist of transition alumina phases plus non-crystalline SiO_2 and do not form mullite below 1200°C.[8] The nature of so-called

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type III mullite precursors is not fully understood: ^{29}Si NMR spectroscopy suggests homogeneous cation distribution[10] but in contrast to type I precursors transition alumina forms at 1000°C instead of mullite while mullite is formed at 1200°C.

Atomic mixing is obviously the clue to understand the crystallization behaviour of mullite from non-crystalline solid state. Spectroscopic methods, such as solid state NMR, yield information on one or two coordination spheres around Al and Si only. Chemical analyses with spatial resolution on nanometer scale have to be ruled out in case of the highly porous gel materials. Thus, the best way to provide a correlation between unmixing effects in non-crystalline alumino silicates and the crystallization behaviour is to introduce a priori well-defined degrees of chemical inhomogeneity ranging from a nanometer to the atomic scale of the precursors. For that purpose alumino silicate films consisting of thin to ultrathin Al_2O_3 and SiO_2 sublayers were vapour deposited by two source evaporation using jumping beam technique.

2. Experimental

2.1. Physical vapour deposition of alumino silicates

For the deposition of alumino silicate films a 150 kW two-source coater (ESPRI 150, v. Ardenne, Dresden, Germany) was used consisting of separate chambers for loading, preheating and deposition. Process parameters, such as beam power, electron beam movement, jumping frequency and vacuum are computer-controlled. Details of the EB–PVD device are described by Lenk et al.[11] Ingots of 63.5 mm diameter were bottom fed into the crucibles during evaporation to ensure continuous coating deposition. Silica was evaporated from a commercial SiO_2 glass rod, while the alumina ingot was manufactured at DLR laboratories to meet the special requirements of PVD ingots such as good thermal shock resistance, low outgassing and minimum spitting during evaporation.

Experiments revealed that mullite composition (60 mol% Al_2O_3, 40 mol% SiO_2) of the deposited material can be achieved, provided that the electron beam is scanned over the Al_2O_3 ingot three times longer than over the SiO_2 ingot. Si_3N_4 discs and austenitic steel foils, respectively, were used as substrate materials for the alumosilicate deposition. Si_3N_4 was employed since thermal expansion coefficients of mullite and Si_3N_4 are similar, and hence the risk of ablation is minimized. These coatings were used for cross-sectional TEM sample preparation. Alumino silicate coatings deposited on steel substrates, on the other hand, delaminated during cooling and were used as powder for X-ray diffraction and for solid state ^{29}Si NMR spectroscopy. Four series of PVD films were produced under variation of jumping

beam frequencies ranging between 7 and 25 Hz. The substrate temperature during deposition was between 600 and 700°C. Film thickness, deposition rates, jumping beam frequencies and nominal thickness of periodical Al_2O_3/SiO_2 sequences are summarized in Table 1. Bulk chemical compositions of the alumino silicate films were checked by X-ray fluorescence. They range between 50 and 63 mol% Al_2O_3.

2.2. Characterization methods

For X-ray diffraction (XRD) a computer-controlled Siemens D 5000 powder diffractometer with Cu-K_α radiation was used. Transmission electron microscopy (TEM) investigations were carried out by means of a Philips Tecnai F30 electron microscope equipped with a Schottky field emission gun and an Oxford EDX system. Cross-sectional TEM specimen preparation was performed as described by Strecker et al.[12] NMR investigations were focussed on ^{29}Si since the ^{29}Si NMR spectrum is affected significantly by the next-nearest atoms surrounding Si and hence information on mixing or unmixing can be achieved. ^{29}Si MAS NMR spectra were obtained by means of a Varian 400 spectrometer. Typical sample spinning speed was 11 kHz. Data processing and spectra deconvolution was carried out at a Sun Sparc station. The ^{29}Si spectra were acquired at 79.4 MHz using a 90° pulse of 3 µs and a recycle time of 600 s. The spectra were referenced to tetramethylsilane.

3. Results and discussion

3.1. As-deposited films

All alumino silicate films produced by vapour deposition under the varying EB–PVD conditions are X-ray amorphous. This is reasonable since the substrate temperatures (600–700°C) are far below the crystallization temperature of non-crystalline alumino silicates (950–980°C). The same is true for alumino silicate films synthesized by reactive sputtering,[7] while alumino silicate coatings produced by CVD with substrate temperatures of $\geqslant$1000°C are consequently crystalline.

Cross-sections of the PVD films investigated by transmission electron microscopy (Fig 1a–c) reveal a sequence of periodical contrasts occurring perpendicular to the deposition direction of series 2 (thickness of double layers $\Delta \approx 9$ nm) and series 3 ($\Delta \approx 5$ nm) while series 4 ($\Delta \approx 2$ nm) appear to be homogeneous (see Table 1). Samples of series 1 could not be prepared for cross-sectional TEM observation due to delamination from the substrate. Contrast periodicities observed in series 2 are 8–10 nm thick while those of series 3 are ≈ 5 nm thick. This corresponds well with the calculated thicknesses of the respective Al_2O_3/SiO_2 double layers. It is noteworthy
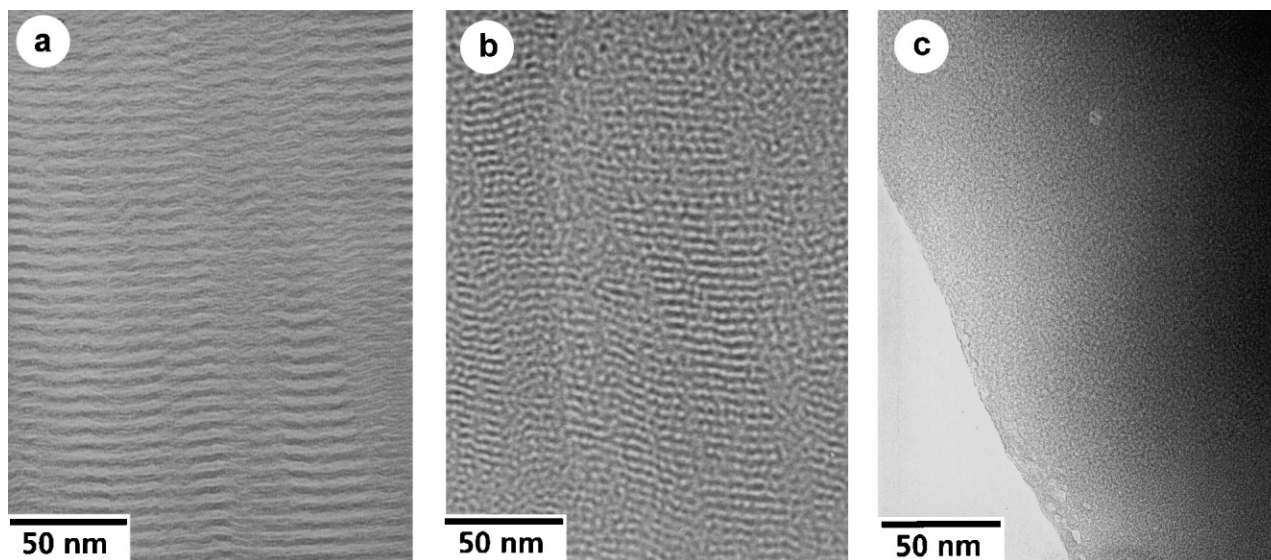
Fig. 1. Cross-section transmission electron micrographs of physical vapor deposited alumino silicate double layers: a, series 2; b, series 3; c, series 4. Periodical contrast modulations are visible in a and b corresponding to the nominal thicknesses of Al_2O_3/SiO_2 double layers of 9 and 5.5 nm, respectively.

Table 1
Experimental conditions of electron beam physical vapour deposition (EB–PVD) runs

	Series 1	Series 2	Series 3	Series 4
Film thickness (μm)	70	75	30	29
Average deposition rate (nm/s)	190	125	75	50
Jumping beam frequency (Hz)	7	14	14	25
Nominal thickness of Al_2O_3/SiO_2 double layer (nm)	27	9	5.5	2

that the periodic contrast modulations are influenced strongly by the focussing conditions, i.e. dark areas in underfocussed images become bright when overfocussed and vice versa. As the wavelength of the contrast modulation corresponds to the calculated thicknesses of a Al_2O_3/SiO_2 double-layer, it can be assumed that the observed bright/dark contrasts are caused by compositional variations. To check this suggestion an EDX line scan perpendicular to the observed contrast layers was performed on a sample of series 2 (Fig. 2). The line scan reveals that the alumino silicate PVD film consists of separate nanosized Al_2O_2- and SiO_2-rich layers.

Due to the limited spatial resolution of the EDX analyses, however, no clear information on the absolute compositional values and on possible chemical gradients between Al_2O_3 and SiO_2 can be obtained from TEM investigations. For that, ^{29}Si MAS–NMR spectroscopy was employed, since the position of the resonance provides a sensitive measure of the average chemical environment of Si-atoms: the ^{29}Si NMR signal centers at ≈110 ppm in case of fully polymerized silica, i.e. if the 4 next nearest neighbours (NNN) of a silicon atom are silicon atoms. If the surrounding silicon atoms

are gradually replaced by Al, the ^{29}Si resonance shifts downfield to achieve ≈90 ppm if all next nearest silicon atoms are substituted by Al.[13]

The spectra obtained from series 1 (≈30 nm SiO_2/Al_2O_3-double layer thickness), series 3 (≈5 nm SiO_2/Al_2O_3-double layer thickness), and series 4 (≈2 nm SiO_2/Al_2O_3-double layer thickness) are shown in Fig. 3: all spectra are very similar and exhibit a resonance in the 108 ppm region. The peak profiles, however, are slightly assymetric indicating a resonance of minor intensity in the 90–100 ppm region, being typically for a high number of Al atoms as NNN of Si. Deconvolution of the assymetric resonances into 2 signals centering at ≈108 and at 90–100 ppm, respectively, results in a peak area ratio of ≈9/1. This means that virtually pure SiO_2 layers occur in all EB–PVD aluminosilicate films investigated. The 10% fraction of Si sites partially surrounded by Al is interpreted in terms of the interface structure between silica and alumina layers, taking into account that the multilayer thickness is in the nanometer range. The occurrence of Al-free SiO_2 layers in sample 4 with the ultrathin (≈2 nm) Al_2O_3/SiO_2 double layers indicate that no atomic mixing took place during deposition. Atomic mixing during two source jumping beam PVD has to be expected, only if evaporation of source 1 continues, although the electron beam has moved to source 2 and causes evaporation there. Evaporation of ceramic ingots, however, stops very rapidly after removing the electron beam,[2] and vapor mixing can only be expected if jumping beam frequencies are very high. The highest frequency used in our study (25 Hz) obviously is not sufficient to produce atomic mixing. From that, freezing rates of the ingot surfaces less than ≈40 ms can be estimated.
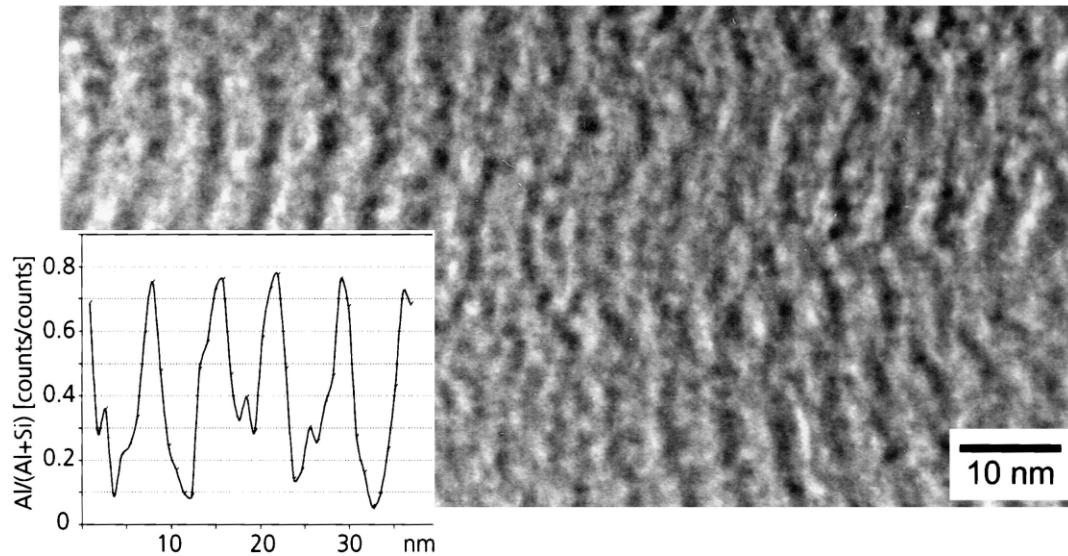
Fig. 2. Cross-section transmission electron micrographs of physical vapor deposited alumino silicate double layers (series 2) in high magnification with EDX-line scan perpendicular to the observed contrast modulations. EDX profile yields evidence for periodical chemical variations.
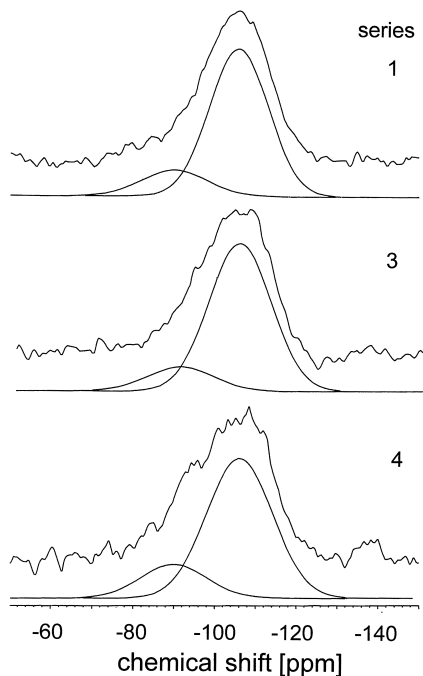

Fig. 3. ^{29}Si NMR spectra of physical vapor deposited alumino silicate double layers of series 1, 3, and 4 (nominal thicknesses of Al_2O_3/ SiO_2 double layers are 30, 5, and 2 nm, respectively). The three spectra are very similar showing a main resonance at 110 ppm and a shoulder centering at ≈90 ppm.

3.2. Crystallization behaviour

To study the crystallization behaviour of the amorphous EB–PVD alumino silicate films the specimens of the 4 different PVD series were heat-treated at 1000°C for 1 h in air. The resulting XRD patterns (Fig. 4) shows that only transition alumina has formed in series 1 (30 nm layer thickness) and transition alumina plus minor
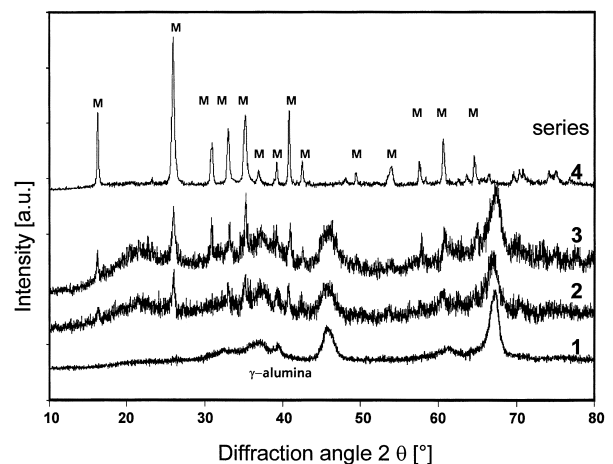

Fig. 4. X-ray diffraction traces of physical vapor deposited alumino silicate double layers after heat-treatment at 1000°C, 1 h: thicknesses of Al_2O_3/ SiO_2 double layers and reaction products are: series 1: ≈27 nm, γ-alumina; series 2: ≈9 nm, γ-alumina plus traces of mullite series; 3: ≈5.5 nm, γ-alumina plus traces of mullite; series 4: ≈2 nm, mullite.

amounts of mullite appear in series 2 and 3 (9 and 5 nm layer thickness, respectively). Only mullite formation has been observed in samples of series 4 (≈2 nm layer thickness). Above 1200°C the transition alumina phase in PVD series 1 to 3 disapears and mullite has been formed instead (Fig. 5), in a similar way as described for diphasic gels[8].

While the crystallization behaviour of samples 1 to 3 corresponds to that of diphasic (type II) mullite precursors, that of sample 4 corresponds to single phase (type I) mullite precursors. This is a very interesting observation since samples of series 4 actually are not single phase but diphasic on a nanometer scale. As a possible explanation we believe that mullite crystal-
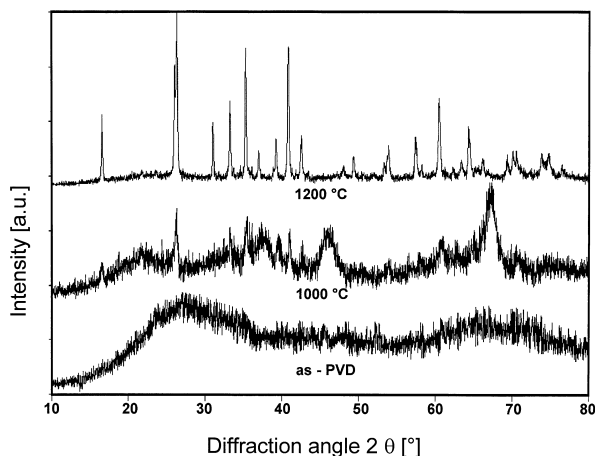
Fig. 5. X-ray diffraction traces of physical vapor deposited alumino silicate series 2 double layers (thickness ≈9 nm) as deposited and heat-treated at 1000 and 1200°C (1 h). Note that predominantly γ-alumina is formed at 1000°C while mullitization occurs at 1200°C only.
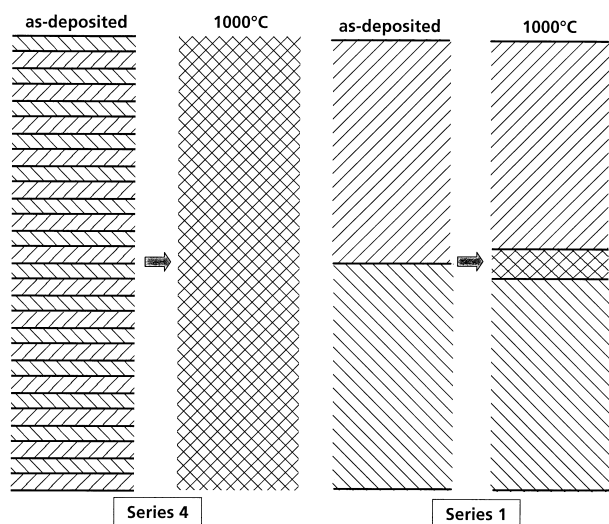

Fig. 6. Schematic view of the interdiffusion-induced homogeneization of Al_2O_3/SiO_2 double layers prior to mullitization: ▨ SiO_2, unmixed; ▧ Al_2O_3, unmixed; ▩ Al_2O_3 and SiO_2 homogeneously mixed.

lization is controlled by interdiffusion-induced chemical homogeneization between adjacent Al_2O_3 and SiO_2 layers, but also by a specific homogeneization volume which is necessary for mullite nucleation (see Fig. 6).

Provided the thickness of interdiffusion zones at the Al_2O_3/SiO_2 interface before crystallization is in the same order of magnitude as the thinnest double layer thickness (2 nm), then complete atomic mixing throughout the PVD film of series 4 is achieved. In that case both conditions, homgeneous chemical mixing and the required volume for stable mullite nuclei are achieved and complete mullite formation is observed at 1000°C. Relationships are completely different in sample 1, where the ultrathin zones of atomic mixing are separated by about 25 nm thick unmixed Al_2O_3 and SiO_2 layers. In that case the extension of the homogeneized

zones (≈1–2 nm) is believed to be below the critical size of a mullite nucleus, taking into account that stable growing mullite nuclei should be at least several unit cell dimensions in size.

Our experiments clearly show that the homogeneity of non-crystalline aluminium silicates required for direct mullite crystallization at 1000°C is not necessarily on an atomic scale but on a nanometer scale (between 2 and 5 nm).

Acknowledgements

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