FTIR and XPS Studies on Corrosion-resistant SiO_2 Coatings as a Function of the Humidity during Deposition

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The degradation of SiO_2 coatings deposited on alloys by metal organic chemical vapour deposition (MOCVD) in sulphidizing high-temperature environments is determined by delamination and crack formation. With increasing water concentration during deposition, the crack density in silica decreases and the critical thickness for delamination of SiO_2 coatings increases. This improvement is supposed to be caused by compositional changes in the SiO_2 coating. In this study presence of water and silanol groups as measured by Fourier transform infrared spectroscopy (FTIR) and the Si:O ratio as measured by XPS are discussed in relation to the protective properties. The FTIR measurements show that the coatings deposited in more humid environments contain more silanol groups and have lower stress levels. The coatings obtained under all deposition conditions consisted of stoichiometric $SiO_{2.0}$ as determined by XPS. The presence of silanol groups reduces the viscosity of the coating, and stress relaxation by viscous flow becomes enhanced, thereby improving the coating performance.

INTRODUCTION

Amorphous silica coatings can be deposited by metal organic chemical vapour deposition (MOCVD) in order to protect alloys against high-temperature corrosion. In previous work[1] the corrosion resistance of these coated alloys in a coal gasification environment is reported. It is found that delamination of the coating from the alloy and crack formation in the coating are the main degradation mechanisms. Both processes are induced by large mechanical stresses in the coating. The difference in thermal expansion coefficient between the substrate and coating has been mentioned as a main source for stress development in the coating upon cooling.[2] Vuorinen and Karlsson[3] observed severe cracking of a CVD Al_2O_3 coating and a loss of adherence, both caused by volume contraction due to the $\kappa \to \alpha$ phase transformation during heating. During deposition, stresses might also be introduced when other phases and compounds are incorporated.[4,5]

Several techniques have been used to monitor the stress generated in ceramic coatings on alloys. Among these, XRD[6–8] is the most frequently used method for crystalline materials. A bending beam method[9–11] has been used to measure the curvature of coated specimens due to cooling or heating. Fourier transform infrared spectroscopy (FTIR)[4,5,12] has mainly been used to study the stress development in amorphous materials, where XRD methods cannot be used. Desu[5] showed, by using the FTIR method, that the intrinsic stress in SiO_2 films deposited by MOCVD increased with either decreasing deposition temperature or increasing deposition pressure. Post-deposition high-temperature heat

treatments decreased significantly the intrinsic stress in silica films. The structure of as-deposited MOCVD SiO_2 films can be regarded as that of fused quartz with elastically deformed Si–O–Si angles, and they were found to be highly stressed.[13] Annealing at high temperatures relieved the distorted Si–O–Si bonds and relaxed the stresses in the films. The properties of the annealed coatings approached those of fused silica for annealing temperatures around 1273 K. The presence of silanol groups in the coating led to a lower activation energy of stress relaxation and, hence, coatings less susceptible to cracking and delamination were obtained. Morssinkhof[4] and Haanappel[12] used FTIR to study the stress levels in amorphous Al_2O_3-coated alloys as a function of several deposition parameters and a post-deposition anneal.

Pou et al.[14] showed that the density of SiO_2 coatings grown by CVD was a function of the process parameters and varied between 1.5 and 2.1 g cm^{-3}. The coatings with a low density did not crack, whereas high-density coatings already started to crack at 723 K. The change in density was supposed to be caused by the presence of suboxides (SiO_{2-x}). Most analytical techniques are not suited for determination of the Si:O ratio due to charging (SIMS), low lateral resolution (SEM/ EDX) or poor quantification (SNMS). A useful method with good quantification, high lateral resolution and not suffering from charging is XPS, measuring both binding and kinetic energies, as proposed by Wagner et al.[15]

In a previous publication[1] it was reported that specimens prepared without water in the reactive vapour are covered with a dense sulphide network after exposure to the mixed sulphidizing/oxidizing coal gasification environments. Coatings prepared with water vapour concentrations above 0.36 vol.% are crack free. Moreover, addition of water during the deposition of SiO_2

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coatings not only improves the crack resistance but also the resistance against delamination. In this work, FTIR and XPS are used to reveal the mechanism by which the humidity influences the coating structure and performance.

EXPERIMENTAL

Deposition of the SiO₂ coatings

The SiO₂ coatings were applied on several alloys by MOCVD using diacetoxydi-*t*-butoxysilane (DADBS) as precursor. The experimental details of the applied technique and equipment are described elsewhere.[16,17] As was shown there, the deposition process could be modified by adding H_2O to the process stream by passing a part of the diluting gas stream through a water saturator kept at 276 K for low water concentrations, or at 300 K for high water concentrations. Furthermore, it should be pointed out that the DADBS concentration in the gas phase was kept constant for all experiments. The MOCVD process conditions are given in Table 1.

Table 1. The conditions used to deposit the SiO₂ coatings

Parameter	Value
Deposition temperature (K)	833
Saturator temperature (K)	353
N₂ flow through DADBS (l h⁻¹)	24
Dilutant flow (l h⁻¹)	24
Water concentration in vapour (vol.%)	0–1.66
Deposition pressure (atm)	1

Substrates

Incoloy 800H and silica were used as substrates. Incoloy 800H is a commercially available Fe-based high-temperature alloy with 19.9 at.% Cr, 31.7 at.% Ni, 0.7 at.% Mn, 0.7 at.% Ti, max. 0.5 at.% Si and max. 0.08 at.% C. Prior to deposition, the Incoloy 800H substrates were subjected to an annealing, polishing and cleaning procedure. The annealing procedure consisted of heating for 1 h at 1373 K, water quenching, heating

for 1 h at 1223 K and further water quenching. The specimens were polished subsequently on 25, 6, 1 and 0.25 μm diamond paste. Finally, the substrates were rinsed for 10 min in ethanol (P.A.), etched for 15 min in an ethanol-based solution of 5% 3 M HNO₃ and rinsed for 10 min in ethanol (P.A.). The silica specimens were XRD-amorphous and before deposition rinsed for 10 min in ethanol (P.A.).

Analysis techniques

The FTIR measurements were performed with a Nicolet 20 SX FTIR spectrometer at an oblique angle. Because the Incoloy 800H specimens were not IR-transparent, a diffuse reflectance cell (Fig. 1) was used during all measurements. The thickness of the coatings was always 1.7 ± 0.1 μm, to eliminate stress related to coating thickness.

The XPS measurements were performed with a Kratos XSAM 800, using an Mg 15 kV/15 mA x-ray source (1253.6 eV). The Si KLL Auger electrons at 1608 eV were generated by the bremmsstrahlung of the radiation.[15] The peak positions of both Auger and XPS were recorded in a slow scan (20 eV min⁻¹).

RESULTS AND DISCUSSION

Possible explanation of the water effect

The improved behaviour of SiO₂ coatings by the addition of water can be caused by several factors:[5,14]

(1) The Si:O ratio is a function of the humidity of gas in which the SiO₂ coatings were produced, and suboxides with other mechanical and chemical properties might be formed;

(2) the number of H_2O and/or OH groups in the coating is altered, whereby the relaxation of the coating by viscous flow is enhanced and final stress levels in the coating are lowered;

(3) the density of the coating is different.

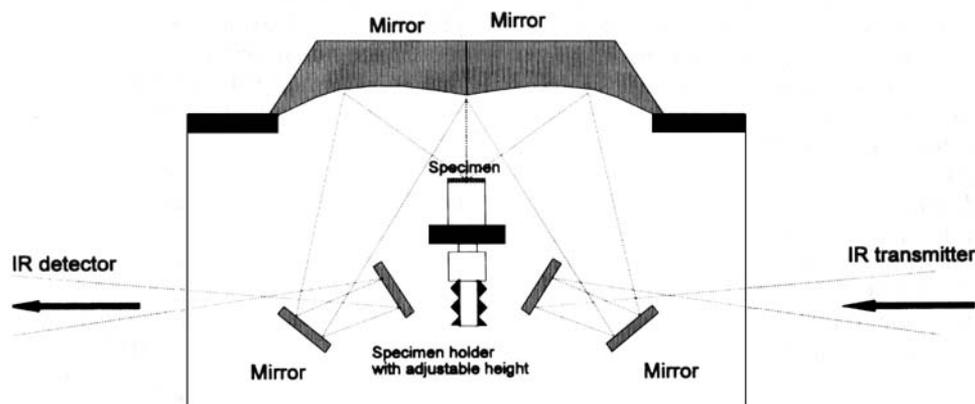The relative influence of these mechanisms was studied by measuring the OH content of the coating by FTIR

Figure 1. Schematic representation of a diffuse reflectance cell used for the FTIR measurements.

and also the Si : O ratio, the specific mass of the coating material and the presence of suboxides by XPS.

The H$_2$OOH ratio as measured by FTIR

In the FTIR spectra of silica coatings deposited on silica substrates, no peaks can be detected below 2000 cm^{-1} because the silica substrate absorbs the IR light in that region. However, in these spectra, peaks of the silanol group and water groups are strong, whereas they are difficult to recognize in spectra of SiO$_2$ deposited on Incoloy 800H. Information on the specific SiO$_2$ peaks can be obtained from the SiO$_2$/Incoloy 800H spectra.

The SiO$_2$/SiO$_2$ spectra (Fig. 2) show that for specimens prepared with increasing humidity during deposition, the water peak between 3000 and 3500 cm^{-1} becomes less significant and the silanol peak at 3670 cm^{-1} becomes more intense. This means that the OH : H$_2$O ratio in the coating becomes larger at higher H$_2$O pressures in the gas. This can be explained by a shift to the left of the equilibrium of the last reaction step of the decomposition of DADBS, in which water molecules and silica are formed[18]

$$Si-OH + HO-Si = Si-O-Si + H_2O \qquad (1)$$

From the SiO$_2$/Incoloy 800H spectra (Fig. 3) the characteristic SiO$_2$ peaks, like the Si–O–Si stretching (1040 cm^{-1}) and the Si–O–Si bending (820 cm^{-1}) frequencies, can be recognized. When stresses are present in the coating, the Si–O–Si bond angle is distorted. As shown by Galeener,[19] such a distortion is directly

Figure 3. The FTIR spectra measured for amorphous silica coatings deposited on Incoloy 800H as a function of the water concentration during deposition.

related to a change in wavenumber (ω) of both stretching (s) and bending (b) mode. A decreasing stress in the coating is accompanied by a shift of the Si–O–Si stretching band to higher frequencies and a shift of the Si–O–Si bending band towards lower frequencies.[5,13] From our results, a slight shift of both the stretching band (towards higher frequencies) and the bending band (towards lower frequencies) with increasing water concentration during deposition is observed (Fig. 4). However, the shifts might also be caused by the presence of silanol groups. The position of the 0% water specimens can be used to distinguish between the two possible theories, because the 0% water measurement concerns a coating of thickness $\sim$1.0 μm, because a 1.7 μm specimen would show cracks. The stress in this coating should be lower than in a 1.7 μm thick coating. This means that, compared with the 0.2% water specimen, the stretching band should be at a higher frequency and the bending band at a lower frequency. However, when the position of the peaks is due to a chemical shift, the stretching band should be at a higher frequency and the bending band at a lower frequency than for the 0% water specimen. For the 0% water specimen the stretching band is found at a higher frequency and the bending band at a lower frequency (Fig. 4), so it is reasonable to conclude that the shifts in Si–O–Si vibrations are caused by the stress level of the coating.

Moreover, the FTIR measurements show that no organic impurities, such as SiCH$_3$, Si–O–C$_2$H$_5$ etc., are present in the coating, in contrast with the results presented by Mukherjee and Evans.[20] The absence of carbon-containing groups in the coating supports the idea that during deposition the carbon-containing groups are split off by gas-phase reactions.[19]
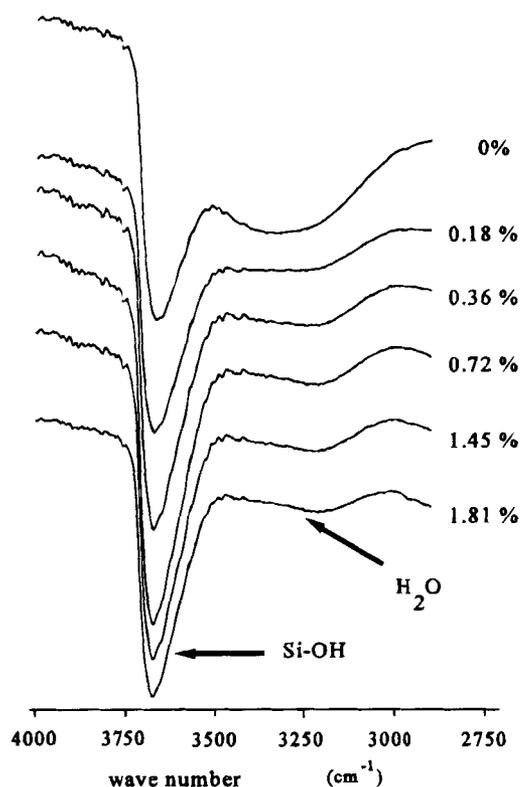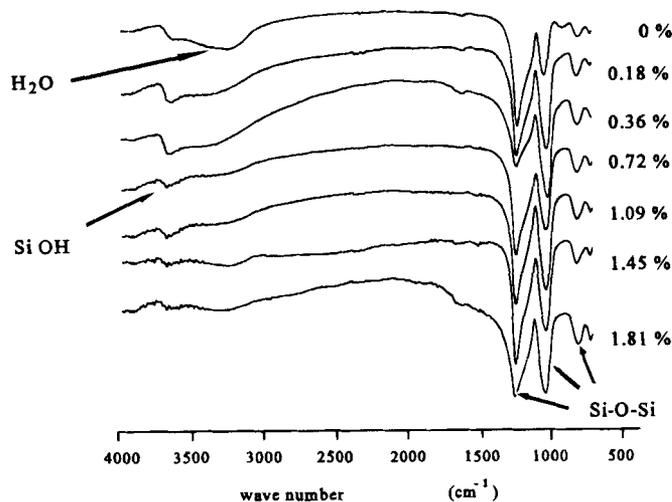
Figure 2. The FTIR spectra measured for amorphous silica coatings deposited on silica as a function of the water concentration during deposition.

The Si : O ratio as measured by XPS

The Si : O ratio of the deposited films was studied by XPS. First, complete spectra of the samples were
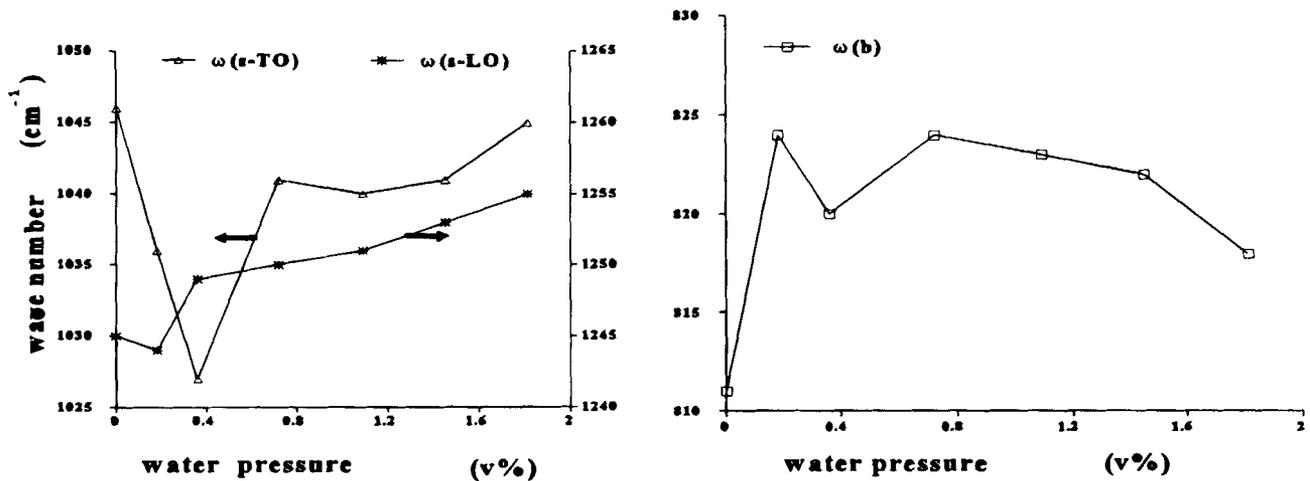
Figure 4. The position of the Si–O–Si peaks of amorphous silica on Incoloy 800H as a function of the water concentration during deposition.

recorded (Fig. 5). These spectra show that no inorganic impurities are present in the coating. Although only surface compositions are measured by XPS, it is assumed that these values do not differ much from the bulk composition of the coating because MOCVD coatings are known to be very homogeneous in composition throughout the coating.[4] When the results of the 1.0 μm thick 0% water specimen are compared to the other 1.7 μm thick specimens, indeed no large differences are observed.

For the purpose of determination of the stoichiometry of the SiO_2, detailed spectra of the O 1s, O KLL Auger, Si 2p and Si KLL Auger peaks were recorded (Table 2). The modified Auger parameter (α') of silicon and oxygen can be calculated on the basis of the position of these peaks, as follows[15]

$$\alpha' = \alpha + h\nu = KE(\text{Auger}) + BE(\text{photoelectron}) \quad (2)$$

where α is the Auger parameter, $KE(\text{Auger})$ is the kinetic energy of the Auger electron and

$BE(\text{photoelectron})$ is the binding energy of the photoelectron. The modified Auger parameter is independent of charging, because charging effects to the kinetic energy and the binding energy are equal and opposite and can therefore be used to describe the properties of coatings on different substrates.

The measured oxygen α' value (Table 2) remains unchanged upon the addition of water during deposition. This means that the ordering of SiO_4 tetrahedra is not changed by the addition of water. From the ratio of the peak areas calibrated on the standard Si/SiO_2 specimen (see Table 2), the Si : O ratio is calculated. This Si : O ratio is not affected by the addition of water. Therefore, it can be assumed that the presence of suboxides, which might alter the density and corrosion properties and their possible influence on the stress levels can be neglected. Further evidence for the absence of suboxides is the fact that the full width at half-maximum (FWHW) of the silicon peak is almost constant. When suboxides are present the Si FWHM is reported to be 2.5 eV.[21] In
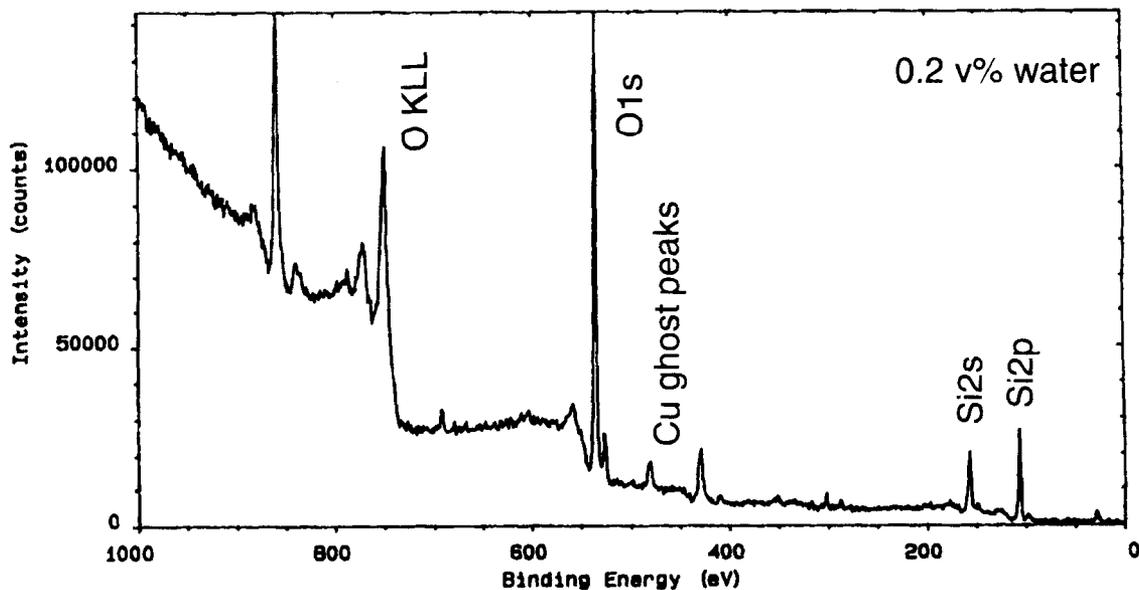

Figure 5. A typical XPS spectrum of SiO_2-coated Incoloy 800H.

Table 2. The XPS and modified Auger parameters of SiO_2 coatings deposited by MOCVD as a function of the water concentration in the DADBS vapour (XPS values not corrected for charging)

Specimen	Layer thickness (μm)	Si 2p (eV)	Si α′ (eV)	O 1s (eV)	O α (eV)	Si 2p FWHM (eV)	O 1s FWHM (eV)	x in SiO_x
0 vol.% H_2O	0.94	107.7	1711.6	537.0	1038.6	2.1	2.2	1.96
0.36 vol.% H_2O	1.62	107.1	—	536.3	1036.6	2.1	2.1	—
0.9 vol.% H_2O	1.60	107.6	—	536.8	1039.6	2.1	2.1	—
1.45 vol.% H_2O	1.70	106.9	—	536.0	1039.5	2.1	2.1	—
1.81 vol.% H_2O	1.74	107.1	1711.6	536.4	1039.6	2.1	2.1	1.96
SiO_2/Si	Thermally	104.3	1711.5	533.4	1039.4	2.1	2.0	2.00

order to compare our results with values found by other authors, the Si α value has been measured for two specimens (0 vol.% and 1.81 vol.% H_2O). The measured O and Si α values are comparable with those of oxidized silicon.[15] Miller and Linton[22] showed that the oxygen Auger parameter of thermally grown relatively unhydroxylated SiO_2, is 1039.6 eV, and for fully hydroxylated SiO_2 this parameter is 1039.3 eV. More hydroxyl groups in the coating should thus lead to a lower value of the Auger parameter. This decreasing tendency is not observed in our measurements, probably owing to the fact that only a relatively small number of hydroxyl groups are present in our coatings.

Alfonsetti et al.[23] studied the modified Si Auger parameter as a function of the stoichiometry parameter x in SiO_x. They formulated a β parameter as follows

$$\beta = 1716 - \alpha'_{SiO_x} \text{ (eV)} \quad (3)$$

where 1716 eV is α' for pure (111) single-crystal silicon and $\alpha'(SiO_x)$ is the measured Auger parameter. The β parameter is a direct measure of the shift of the Si_{2p} core level caused by the O atoms. An equation relating the β parameter to the stoichiometry factor x is empirically derived as

$$\beta = 2.25x \quad (4)$$

With these equations it is possible to calculate the stoichiometry factor from the Si Auger parameter. The x value calculated from our measurements is 1.96. Because the error of the calculated stoichiometry value is 0.05,[23] it can be concluded that within the accuracy of these measurements the deposited coating is $SiO_{2.0}$. However, it should be noted that, as discussed before, OH groups are incorporated in the SiO_2 network and the composition should be written as $SiO_2 \cdot y$ OH, with $y \ll 1$.

Discussion of the mechanism responsible for the beneficial effect of water

The addition of water to the metal organic vapour undoubtedly leads to an improved sulphidation resistance due to changed mechanical properties of the layer. The beneficial effect cannot be attributed to a change in stoichiometry or ordering of SiO_4 tetrahedra in the coating, as shown by the XPS measurements. Therefore, the most likely explanation is that, owing to a change in

the equilibrium of the last decomposition step, silanol groups are incorporated in the amorphous silica network. As a result, the viscosity of the coating is lowered and stress relaxation by viscous flow is enhanced.[24] Reduction of the viscosity and thereby lowering of the activation energy of stress relaxation by viscous flow in amorphous silica by the formation of silanol groups (Si–OH) has been demonstrated by Tomozawa.[25] According to Desu,[13] this reduced activation energy allows stress relaxation by viscous flow at relatively low temperatures. It is even possible that stress relaxation already occurs at the temperatures (~833 K) at which SiO_2 coatings are deposited by MOCVD with DADBS as precursor.

CONCLUSION

The protective properties of alloys coated by amorphous SiO_2 are increased by the addition of water during the deposition process. When the water concentration during deposition of the SiO_2 coatings is increased, the crack density and the crack branching decrease and the critical coating thickness and the corrosion resistance increase in both oxidizing and mixed oxidizing/sulphidizing environments. The beneficial effect of water is related to a stress reduction, as demonstrated by FTIR. The number of silanol groups in the coating seem to be very important. The resulting hydoxylated SiO_4 network has a lower viscosity and a lower activation energy for relaxation by viscous flow. As a consequence, at relatively low temperatures stress relaxation by viscous flow becomes possible and overall stress levels in the coating are lower. The composition of all silica coatings deposited at 833 K by MOCVD with DADBS as precursor was always stoichiometric ($SiO_{2.0}$) as determined by XPS.

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