

The impact of plasma enhancement during deposition of carbon containing zirconia films by chemical vapor deposition

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Abstract: ZrO₂ layers are used as hard coatings or as thermal barriers for a variety of applications. ZrO₂ is usually deposited by CVD methods using a precursor consisting of ZrO₂ species surrounded by hydrocarbon ligands in an Ar/O atmosphere. To lower the growth temperature, we combine the CVD process with a plasma activation. This leads to the appearance of crystallinity at lower surface temperature as well as an incorporation of carbon in the films at oxygen sites, so that the crystalline structure of ZrO₂ is preserved, but the electrical conductivity is affected.

Keywords: CVD, PECVD, thermal barrier coatings, zirconia, 3 ω method

1. Introduction

Thermal barrier coatings are an important interface for many applications. These layers are used to manage thermal loads ranging from extreme cases as turbine blades in jet engines to mild conditions as in injection molds in the plastics industry. Here, thermal barrier coatings are used on the inside of the mold, to keep the injected plastic at a high temperature during the plastics forming process. Thereby, the plastics can penetrate more easily in smaller structures of the mold, which lowers the total energy consumption of an injection molding machine since the heat that is stored in the molten plastic granulate is used for a longer time. Given the large amount of produced plastics a day, any energy savings for injection molding processes have a huge impact. The requirements of the barrier coatings are manifold because the surface of the molded plastics part is in direct contact with the thermal barrier and the sheen of the surface is directly affected by the smoothness of the plastic part. In addition, these thermal barrier coatings need to be perfectly electrical insulating and free of pores, because the hot plastics in the injection mold may interact with the steel mold itself and may cause corrosion.

2. (PE)CVD deposition of zirconia

One typical material for this application is zirconia, which is often stabilized with a small concentration of incorporated Yttrium. The standard deposition method is the use of a ZrO₂ containing metalorganic precursor that is made volatile by tuning the ligand sphere to match the targeted properties in a chemical vapor deposition (CVD) process. In this case, the all-oxygen coordinated heteroleptic bis(isopropoxide)bis(tert-butylacetoacetate) zirconium [Zr(OⁱPr)₂(tbaac)₂] precursor [1] is evaporated in an oxygen containing atmosphere and decomposes upon impact at a heated surface into reactive surface species to form a crystalline ZrO₂ layer by surface reactions with the oxygen co-reactant. Unreacted precursor and by-products desorb from the surface and are carried out of the reactor by the carrier gas. This process requires temperatures of typically 700 K to 800 K. At these high growth temperatures any hardened steel will start to be softened, which limits the application of the CVD process. The

growth rate in the CVD process is governed by a temperature window. At low temperatures the precursor may not decompose upon surface impact. However, at too high temperatures, the residence time of the precursors at the surface is so small that it desorbs before its decomposition and thus film growth won't take place. While metalorganic precursors exhibit a rather low temperature window for the deposition of ZrO based layers compared to conventional precursors, these temperatures might still exceed the limits of steel molds.

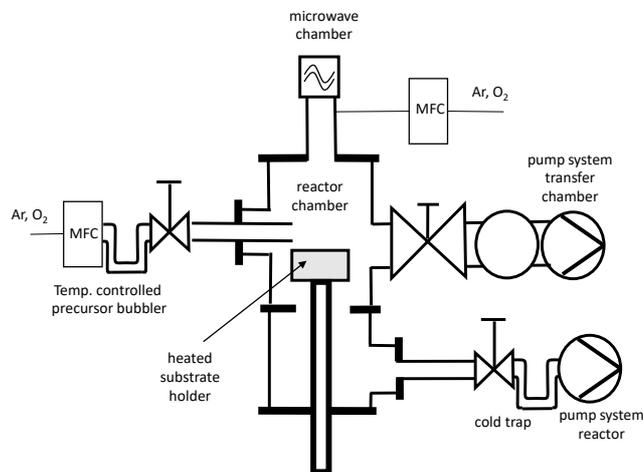


Fig. 1. (PE)CVD setup

The strict relationships between growth precursor and temperature window for deposition can be altered by combining the CVD process with a plasma process. In a PECVD (plasma enhanced chemical deposition) process, the plasma can support the activation process of the precursor or the plasma dissociates the admixed oxygen in the gas phase, so that oxygen atoms react at the growth surface rather than only the molecules. Both aspects affect film growth and change the temperature window as well as possibly the film structure. This concept is explored here, by employing a zirconia CVD process and enhancing it with a remote plasma process to activate the oxygen and the precursor molecules.

3. Experimental Setup and Diagnostics

The evaporated metalorganic precursor $[Zr(O^iPr)_2(tbaoac)_2]$ (details see [1]) is transported into the reaction chamber by a nitrogen-flow of 50 sccm at pressures of about 100 Pa (see Fig. 1). A ZrO_2 layer is deposited onto a heated substrate in the centre of the chamber with a growth rate of several 100 nm/h. To influence and improve the reaction chemistry, a microwave plasma source is mounted opposite to the substrate surface. The microwave plasma source is operated with oxygen gas flows of 50 sccm at powers of ~ 750 W. This gas flow is not changed between CVD and PECVD-processes to increase the comparability.

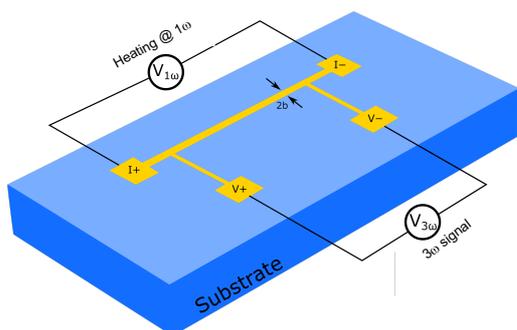


Fig. 2. Scheme of the 3ω method

The discharge interacts with the incoming precursor molecules with the aim to reduce the reaction temperature and change the deposition properties. During this process, the growth rate is monitored by in-situ ellipsometry to obtain insights into chemical kinetics and mass transport phenomena. From these data, also the substrate temperature can be deduced. The deposited layers are characterised with respect to stoichiometry and crystallinity, using X-ray photoelectron spectroscopy (XPS) as well as X-ray diffraction (XRD).

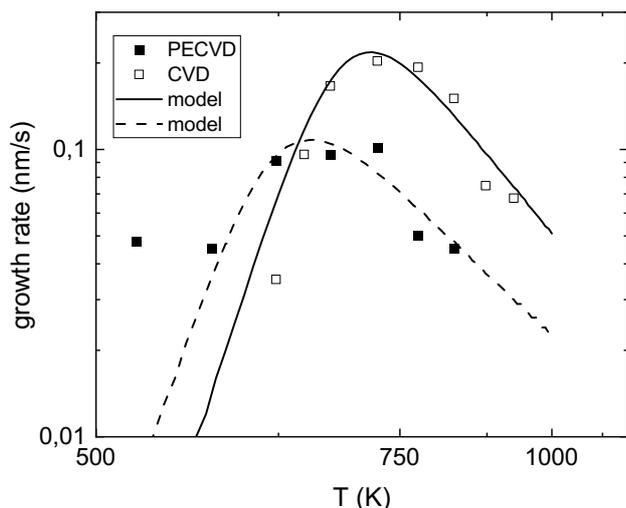


Fig. 3. Temperature dependent growth for the PECVD and CVD case. The solid and dashed lines denote an adsorbed layer model.

The thermal properties of the coatings are analysed ex-situ by the 3ω method [2]. This method can be applied to bulk amorphous solids and crystals as well as to amorphous films tens of microns thick. A thin electrically conductive gold strip is deposited onto the specimen to measure its thermal conductivity (see Fig. 2). The gold strip serves both, as a heater and as a temperature sensor, respectively. Joule heating at a 2ω frequency occurs when an AC current with angular modulation frequency ω is applied to the gold strip. The generated thermal wave diffuses into the specimen. This causes a modulation of the resistance at 2ω due to the temperature dependence of the resistance. The voltage drop along the gold strip contains a contribution from a third harmonic that depends on the modulated temperature rise of the heater and could be used to calculate the thermal conductivity of the sample. Before applying the 3ω method to the ZrO_2 layers the method is benchmarked with reference samples with known thermal properties.

4. Results and discussion

Film growth is analyzed with respect to its temperature dependence (see Fig. 3) to identify activation energies. For this, an adsorbed layer model [3] is defined with a balance equation for the coverage of an adsorbed layer of precursor molecules. The measurements reveal, that the activation temperatures for film growth decreases slightly for the PECVD case. Also the activation temperature for desorption is significantly lowered for the PECVD case. This could be explained with the fragmentation of the precursor molecules, where already a few ligands have been eliminated. A smaller molecule might be more weakly bound and thus the activation energy for desorption is smaller.

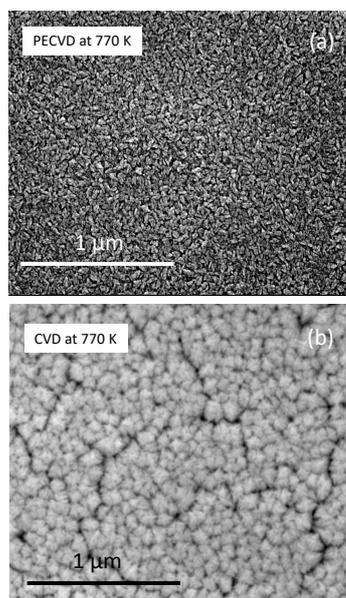


Fig. 4. SEM micrographs of films deposited with the PECVD (a) or the CVD (b) process at 770 K substrate temperature

Fig. 4 shows SEM micrographs of films deposited at 770 K using the PECVD method (a) and the CVD method (b). Although both show crystalline structures, the PECVD films exhibit much smaller grains with a diameter of typically 30 nm, whereas the samples from the CVD process show larger grains in the range of 70 nm, which are also better connected. Apparently, the growth precursor in the PECVD process is more reactive leading to enhanced nucleation of new grains and thus to a large number of small grains. This is in contrast to the CVD process, where the less reactive precursor induces a smaller nucleation rate and thus a bit larger grains eventually.

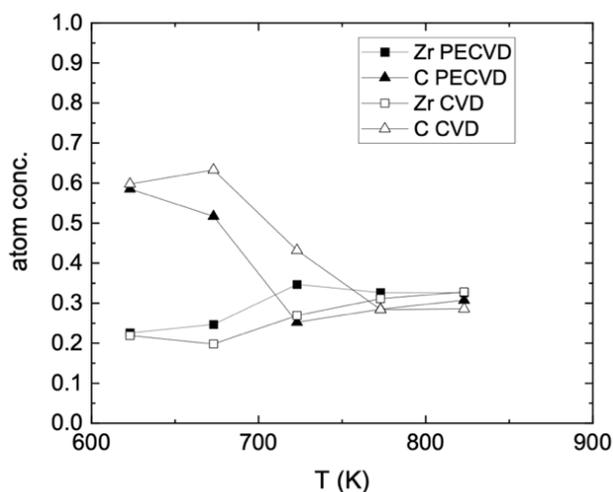


Fig. 5. Composition of the CVD and PECVD films in atomic fractions for the CVD and PECVD (b) case.

XPS is used to analyze the composition of the films by depth profile sputtering to determine the carbon concentration within the film. One can see (Fig. 5) that at high temperature a stoichiometry of $\text{ZrO}_{1.4}\text{C}_{0.7}$, which is consistent with a structure where 30% of the oxygen sites in a ZrO_2 crystalline structure are occupied by carbon. Even at a high temperature, the film is not carbon free. This might be related to the limited supply of oxygen molecules with respect to precursor molecules. The activation of the oxygen by the plasma is also not affecting the carbon concentration at high temperatures.

The thermal conductivity λ_{therm} of the material has been measured ex-situ as a function of temperature using the 3ω method (see Fig. 6). The samples from the PECVD method show a smaller thermal conductivity and thus better thermal barrier properties. λ_{therm} , measured at room temperature, is around 8 W/m/K for the samples deposited at 770 K using the CVD method and between 0.8 and 2 W/m/K for the samples deposited using the PECVD method between 670 K to 870 K. Values of a few W/m/K are also typical for zirconia in general. The thermal conductivity measurements also reveal that λ_{therm} increases at higher temperature for all samples, as being indicative for an activation energy in the thermal transport process. This dependency could be explained

by an electronic component on top of the phonon component in λ_{therm} since carbon containing zirconia is known to be a semiconductor rather than an insulator.

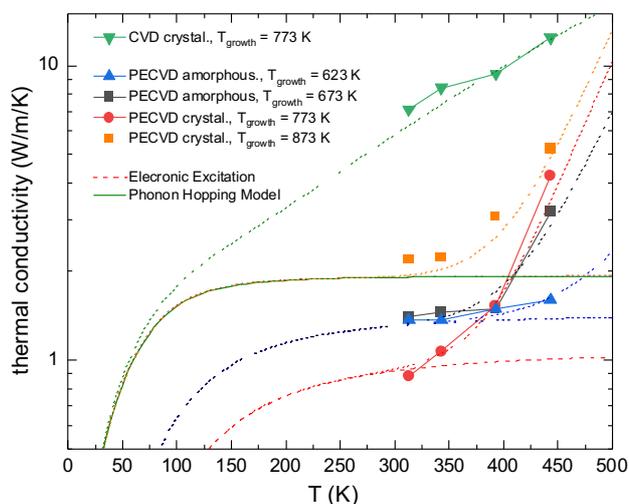


Fig. 6. Thermal conductivity of amorphous and crystalline PECVD films in comparison to crystalline CVD films. The solid lines denote a phonon hopping model for thermal transport, the dashed lines an additional electronic component.

In conclusion, the PECVD process causes the precursor molecules to be transformed in chemically active species already in the gas phase, yielding growth species in the PECVD process which exhibit a five times higher sticking coefficient compared to the CVD process. This in turn also leads to the appearance of crystallinity at lower surface temperature in the PECVD process compared to the CVD process. In addition, carbon is incorporated in the films at oxygen sites, so that the crystalline structure of zirconia is preserved, but the electrical conductivity is affected. The thermal conductivity is similar to pure zirconia. This shows that PECVD can lower the growth temperature and accelerate film growth in these applications.

5. Acknowledgement

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6. References

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