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Control of thickness and morphology of thin alumina films deposited via Pulsed Chemical Vapor Deposition (Pulsed CVD) through variation of purge times

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ABSTRACT

Thin alumina films were deposited onto graphitic carbon fibers at 77 °C by gas phase exposure to sequential pulses of trimethylaluminum and water vapor, each pulse being separated from the subsequent one by a purging pulse of nitrogen gas. By varying the duration of the purging pulse, one can tune the morphology of the deposited film from a gas phase precipitation reaction to deposition controlled by surface saturation. A purge time of 15 s leads to non-uniform and non-conformal films, the fibers at the perimeter of the bundle were coated with a thicker film compared to the fibers inside the bundle. The film deposition rate inside the bundle was about 0.83 nm/cycle, which is much higher than a single alumina monolayer per cycle. This indicates a significant precipitation of alumina from gas phase reactions onto the carbon fibers. With increasing purge time, homogeneity and conformality of the film improved and the variation of thickness from perimeter to inside the bundle decreased significantly. At 30 s purge time, the films were already smooth and conformal, as expected for a deposition controlled by surface saturation, and the deposition rate was 0.34 nm/cycle. Further increase of purge time up to 100 s, did not change the morphology significantly, and led to a deposition rate of 0.27 nm/cycle which is less than expected for a monolayer. Experiments conducted at increased pumping speed gave essentially the same results. The deposition rate observed here in the mode of deposition controlled by surface saturation is higher than commonly reported for Atomic Layer Deposition (which usually is conducted at higher temperatures). Increasing the deposition temperature led to deposition rates in accordance with the values reported for Atomic Layer Deposition.

1. Introduction

In Chemical Vapor Deposition (CVD) a surface is exposed to precursors, more precisely a mixture of gaseous components which react to form a solid deposit on the surface. In principle, the components of the process might react already in the gas phase; however, it is of significant advantage to control the process in such a way that chemical reactions occur only at the solid/gas interface. Even in the latter case we have to distinguish two extremes: if the rate determining factor of the process is the reaction at the surface, one can expect uniform thickness of the deposited films even deep down in trenches e.g. in the preparation of a capacitor in a microelectronic circuit or deep in porous structures e.g. a porous membrane or a bundle of fibers. However, if the rate of the process is controlled by the diffusion of the precursors to the surface, one obtains a non uniform film thickness, especially if there is a non uniform diffusion path from the source of the precursors to the surface. Thus, a process controlled by the surface reaction rate is preferred. However, any process controlled by the surface reaction rate eventually becomes controlled by diffusion if the diffusion path gets extensively non uniform, e.g. if the surface exposes very deep trenches or if one desires to coat thick bundles of fibers. One elegant way to obtain uniform film thicknesses even in geometries that require deep infiltration is Pulsed Chemical Vapor Deposition (Pulsed CVD) [1–3], especially Atomic Layer Deposition (ALD) [4]. In this process there are two precursors that are delivered into a reaction chamber sequentially by separate pulses; these pulses are separated by a purging step with an inert gas. One exposure and subsequent purging is called a half cycle; the succession of the two half cycles is one complete cycle. Usually, several cycles are applied subsequently. In the first half cycle the surface is saturated with the first precursor for example with one monolayer of chemically or physically adsorbed molecules. In the second half cycle these molecules react with the second precursor to form a well defined layer of a thin solid film [5]. Purging of the reaction chamber in between the pulses removes all excess of precursors and byproducts after each precursor pulse. The amount deposited may vary between more than a monolayer or a fraction of a monolayer but definitively reaches a surface saturation limit if one exceeds a certain precursor dose and if the duration of the precursor pulse is long enough to allow the precursor to diffuse even into trenches and pores. Further increase of purge time will not affect the amount deposited per cycle. Thus, a

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precursor dose which is above surface saturation limit (with respect to the amount and duration) and a sufficient purge time will deposit a uniform film of a certain thickness in each cycle. In case of Atomic Layer Deposition, saturation occurs due to the formation of covalent bonds and one expects the deposition rate to be equivalent to a monolayer; however, it is usually less than a monolayer due to steric hindrance [6]. If saturation occurs due to physisorption it is possible as well that more than a monolayer of precursor is adsorbed. As long as the film growth is limited by surface saturation and the pumping speed and the flow of the purge gas are sufficient to prevent the mixing of the precursors inside the reaction chamber, the increase of coating thickness per cycle will be uniform and the deposited film will be conformal to the substrate — even if the geometry of the surface is complicated.

Pulsed Chemical Vapor Deposition (Pulsed CVD) may deviate from this principle in two ways: (i) one of the precursors may not be a reagent but a catalyst which triggers a limited deposition of a solid film via reaction of the second precursor. In this case, films of well limited catalyzed growth larger than a monolayer may form per cycle [7]. (ii) If the purge time is chosen rather short, one may observe: (a) the formation of more than a monolayer in a single cycle, (b) diffusion controlled reaction and (c) spontaneous bulk gas phase reaction inside the reactor. Thus, one can expect in Pulsed CVD a deviation from conformal growth upon shortening the purge time further and further. However, Pulsed CVD is also carried out at a low pressure which facilitates surface confined growth due to faster precursor diffusion and slower gas phase reaction rate even though the precursors might mix in the gas phase to a certain extent [8]. High reactivity of the precursors and low deposition pressure might allow to deposit deep into trenches. Thus, by tuning the Pulsed CVD process, one can achieve an optimum deposition behavior and conformal growth at conditions that lead to growth rates of more than a monolayer per cycle.

However, when the precursors are mixed to a large extend, there is a possibility of deposition from bulk gas phase reaction. This increases the deposition rate further, but usually adversely affects the morphology of the deposited films. Surface confined growths always produce smooth, uniform films whereas gas phase precipitation usually deposits rough films and thus should be avoided. In addition, the structure of the deposited film may be influenced by the reaction parameters like temperature, and pressure etc. which might induce a change in the morphology simultaneously with in the deposition.

We are aware of one very carefully done publication comparing pulsed Plasma-Enhanced Chemical Vapor Deposition (PECVD) to Plasma-Enhanced Atomic Layer Deposition (PEALD) onto silicon wafers [9]. In this work it was shown that one can obtain self-limiting growth of alumina in pulsed Plasma-Enhanced Chemical Vapor Deposition. The growth rate per cycle levels off with increasing pulse duration and increases linear with the partial pressure of the gaseous precursor. The extrapolation of the alumina growth rate in pulsed PECVD towards negligible partial pressure of the precursor coincides with the growth rate observed in PEALD.

In our current article, we aim to investigate deposition of thin alumina films onto carbon fibers via Pulsed CVD, especially investigating the transitions between process conditions controlled by surface saturation and conditions that do not rigorously exclude mixing of precursors in the gas phase. The predominant application of such coated fibers will be reinforced composites. Such carbon fibers coated with alumina already have been prepared using sol-gel techniques [10], CVD [11] and ALD [12]. In this context the major focus of attention is uniformity, absence of bridges between fibers and the absence of holes and defects within the coating. Thus, we primarily investigate the morphology of thin films formed by vapor deposition with various purge times while keeping the other parameters constant.

2. Experimental procedures

Tenax HTA 5331 6K, PAN-based carbon fibers (bundles of approximately 6000 fibers, each fiber had a diameter of approximately 7 μm) was purchased from TOHO TENAX. As obtained, the fiber bundles bear a polymeric sizing. This sizing was removed by thermal treatment at 700 °C in N_2 atmosphere. Besides this thermal desizing no other treatment was performed before film deposition. The reaction chamber and sample holder are identical to the one described elsewhere [13]. Briefly, the reactor is a 1 m long steel tube connected at one end to the precursor via computer controlled valves and to the purge gas via mass flow controllers and at the other end to a rotary vane pump (Pfeiffer Vacuum), via another computer controlled valve. 3.6 meter long segments of this fiber were mounted within the reactor onto a fiber holder in such a way that they were oriented longitudinally within the reaction tube and bent by 180° with a bending radius of 5 mm at the ends facing the precursor flow, respectively the pump. Fibers are coated with alumina at a temperature of 77 °C using pulses of trimethylaluminum (98% from Strem chemicals) and of deionized water as precursors in a homebuilt reactor. The supply vessel of trimethylaluminum was heated to 60 °C. The temperature of the water supply was maintained at 50 °C. Two streams of nitrogen were used as carrier for trimethylaluminum and water respectively, and as purge gas, their flow was controlled by two mass flow controllers each set to 20 standard cubic centimeters per minute (sccm). In the first half cycle, the fiber bundle was exposed to trimethylaluminum for 20 s followed by purging the reactor with nitrogen. In the second half cycle it was exposed to water vapor for 20 s followed by purging the reactor with nitrogen. In both exposures the valve in front of the pump was closed, it was opened fully during the purge time. Nominal pumping speed (as specified by the manufacturer) during the purging cycle was 5 m^3/h (Pfeiffer Vacuum, Duo 5, Mod. Nr.: PK D61 705 AA) in most experiments and was increased to 20 m^3/h (Pfeiffer Vacuum, Duo 20, Mod. Nr.: PK D63 021) in a second set of experiments. The purge times after exposure to one precursor were chosen to be identical to the purge time after exposure to the other one. A series of experiments was performed by varying only the purge time with durations of 15 s, 30 s, 45 s, 60 s, 75 s and 100 s, while the other parameters remained unchanged. Coated fibers were annealed using a tube furnace in vacuum.

Scanning Electron Microscopy (SEM) was carried out using a NanoNovaSEM (Philips), directly taking the specimens from the bundles after deposition.

3. Results and discussion

Bundles of carbon fibers were coated with alumina by sequential exposure to pulses of trimethylaluminum and water vapor at reduced pressure and a temperature of 77 °C, varying the purge time. The low deposition temperature is of advantage, first of all because it makes the deposition process gentle to the fiber. Furthermore: at high temperatures, the deposited thin film may already undergo structural rearrangement in situ. Thus, a low deposition temperature helps to observe the morphology in the 'as deposited' state. In addition, the fibers chosen have a corrugated surface. This allows to judge conformality of the deposited films as a function of purge times. In the first half cycle, the fiber bundle was exposed to trimethylaluminum for 20 s followed by purging the reactor with nitrogen. In the second half cycle, it was exposed to water vapor for 20 s followed by another purging. The purge times were varied systematically. The coated carbon fibers were characterized by Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDXS). Elemental analysis of the coated fiber by EDXS revealed in all cases a carbon content and aluminum and oxygen. The carbon content was expected because of the carbon fiber, the presence of aluminum and oxygen confirms the expected alumina film. EDXS results for all kinds of fibers