FINAL REPORT

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on

DESIGN OF INORGANIC WATER REPELLENT COATINGS FOR THERMAL PROTECTION INSULATION ON AN AEROSPACE VEHICLE

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prepared by

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ABSTRACT

In this report, thin film deposition of one of the model candidate materials for use as water repellent coating on the thermal protection systems (TPS) of an aerospace vehicle was investigated. The material tested was boron nitride (BN), the water-repellent properties of which was detailed in our other investigation. Two different methods, chemical vapor deposition (CVD) and pulsed laser deposition (PLD), were used to prepare the BN films on a fused quartz substrate (one of the components of thermal protection systems on aerospace vehicles). The deposited films were characterized by a variety of techniques including X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy. The BN films were observed to be amorphous in nature, and a CVD-deposited film yielded a contact angle of 60 degrees with water, similar to the pellet BN samples investigated previously. This demonstrates that it is possible to use the bulk sample wetting properties as a guideline to determine the candidate waterproofing material for the TPS.

I. INTRODUCTION

Thermal protection systems (TPS) for a reusable space launch vehicle are expected to be a maturation of developed technology. Two materials that are TPS candidates are blankets and tiles, whose major components are silica and alumina [1, 2, 3]. As fabricated, these materials are hydrophilic and without protection can imbibe water, therefore necessitating the TPS to be waterproofed [4]. The waterproofing agents used for this purpose, silane derivatives, though extremely effective for waterproofing, create a hydrophobic coating which decomposes at the high temperatures experienced by the TPS during reentry [4, 5], which requires the TPS to be rewaterproofed after every flight. A prime driver in the new launch vehicle design is operational efficiency. A permanent waterproofed TPS which retains its hydrophobicity after thermal cycling such as repeated reentries, would enhance the efficiency by reducing maintenance time and cost.

The objective of our initial project was to investigate and define factors that control the hydrophobicity of inorganic materials, including the development of a model for characterizing the hydrophobicity of such materials, and to test the water repellency and thermal cycling behavior of selected materials [6]. A suitable water-repllent film would have to be deposited on the TPS by surface-coating techniques [7]. The objective of this report is to present the results of our investigation of using surface deposition techniques to coat silica as a model TPS substrate.

II. BACKGROUND

In our initial project, we tested the thermal cycling behavior of various materials, boron nitride, molybdenum disulfide, talc, and pyrophyllite. All the materials considered belong to the class of materials having layered structures. Talc and pyrophyllite belong to the class of two silica tetrahedral layer (SiO/MOH/SiO) silicate minerals; molybdenum disulfide (molybdenite) is comprised of two layers of sulfur sandwiching a layer of molybdenum ions; and boron nitride possesses a graphite-like structure. In this project, we

tested the thin film deposition of one candidate material, namely boron nitride. The thin film coating of any potential water-repellent material is necessary because of weight considerations of any relaunch space vehicle.

For studying the thermal cycling behavior of the various candidate materials, we used cold-pressed pellets [6]. In most of the materials that were considered, the material was comprised of nonpolar faces and polar edges. The nonpolar faces provide the hydrophobic surface, whereas the edges possess predominantly broken primary bonds which contribute to the hydrophilicity of the material [6]. However, a thin film deposition method should achieve mostly a "face-like" orientation in the coasting. This should then give rise to a predominantly hydrophobic material. A thin-film deposition technique may also produce a surface that is covered mostly by a uniform single phase of that material.

A variety of different techniques could be used to deposit thin films [8, 9, 10], including chemical vapor deposition (CVD), evaporation, sputtering, molecular beam and plasma based methods and laser assisted methods. For this project, two different techniques were used to deposit the material. The first was CVD, and the second was pulsed laser deposition (PLD).

Chemical vapor deposition

CVD can be defined as a process where usually gaseous precursors are introduced into a reactor and a solid material is obtained as a product of a chemical reaction. The schematic of a CVD reactor is shown In Figure 1. The deposition process inside the reaction chamber takes place in three main steps: first, there is transport of the reactants as gases (or liquid droplets) to the substrate followed by an adsorption process; second, a chemical reaction at the surface resulting in the formation of solid product material on the substrate surface; and third, desorption and transport of gaseous product species from the substrate surface.
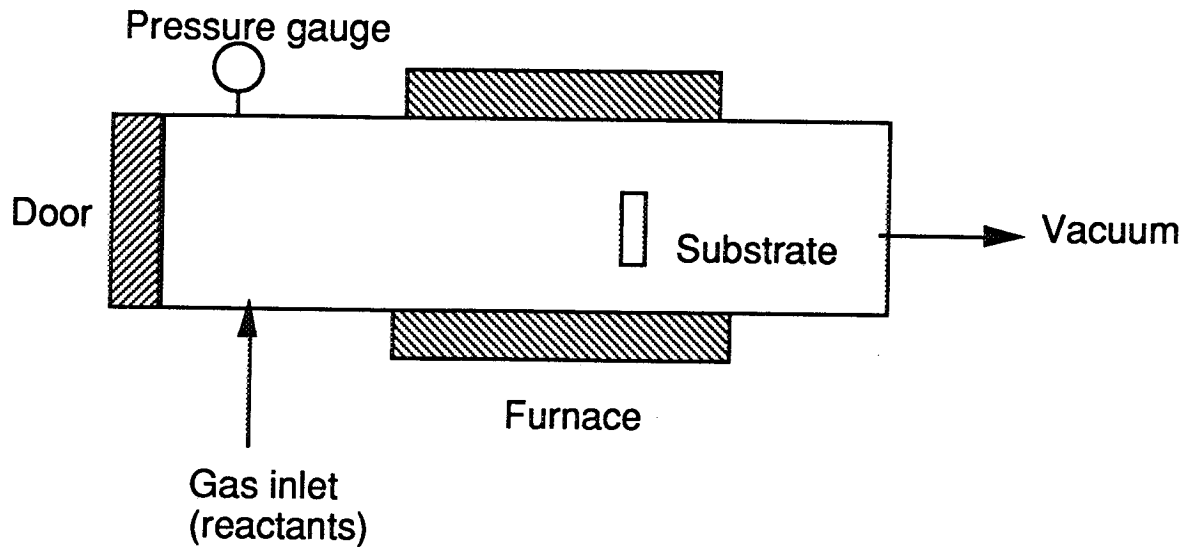
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Figure 1- Schematic of a CVD reactor

A variety of process variables are involved in the thin film deposition method. Of major importance is the chemical nature of the feed material in relation to obtaining the desired deposited material. Operating variables include gas flow rates, the pressure condition inside the reactor, the angle at which the reactant gases are incident on the substrate surface, and finally the substrate conditions, that is the temperature of the substrate and the surface orientation characteristics (the crystal plane that is exposed).

The advantage of CVD is that it gives conformal or uniform coverage over the substrate. A low pressure in the CVD chamber increases the mean free path of the gas molecules so that all of the chemical reaction that takes place in the formation of the solid product occurs mostly on the substrate surface. The final material properties of the film is a function of the starting materials.

For the deposition of boron nitride, a couple of different methods have been reported in the literature. The method we used in our work was that discussed by Levy et al. [11]. The other method which could be pursued is deposition using boron tribromide and ammonia gas with hydrogen as carrier gas. In their work, Choi et al. [12] reported that at temperatures

between 800 °C and 1300 °C, hexagonal boron nitride, which has a graphite-like layered structure, takes place. The key parameters which they found to play an important role in the formation of the desired phase were the total pressure in the system and the relative pressures of the two components. According to them, the optimal operating conditions were attained at a total pressure of 2 kPa at a ratio of ammonia-to-boron tribromide of 3. Derre et al. [13] used a slightly different chemistry that consisted of boron trichloride, ammonia, and hydrogen gas to obtain the boron nitride films. They observed that the mixed carbon-boron nitride films had oxidation stability up to temperatures of 800 °C, where there is formation of boron oxide on the surface. The kind of films that Derre et al. [13] obtained were similar to those by Levy et al. [11].

Pulsed laser deposition (PLD)

In PLD, a laser pulse of energy density between 1 - 5 J cm^{-2} is incident on the target material of interest. Localized evaporation takes place from the target, and the product material (which is mostly in a normal direction to the surface) is transported and deposited onto a substrate. There is a high efficiency of deposition, mostly due to the geometric arrangement of the target and the substrate material. A schematic of the PLD process is shown in Figure 2.

In PLD, a variety of process variables are involved: the temperature of the substrate and its crystallographic orientation, the laser energy density, the pressure inside the reactor, the distance between the target and the substrate, and the number of laser shots used for the deposition.

The nucleation and the growth of the material deposited is linked directly to a phase stability plot of the pressure and the reciprocal of the temperature. Figure 3 shows such a plot for boron nitride [14]. The line in the P - vs.- (1/T) plot indicates the critical conditions required for film formation. The region to the right of the line is the stable region for growth of a boron nitride film and that to the left is the unstable region.
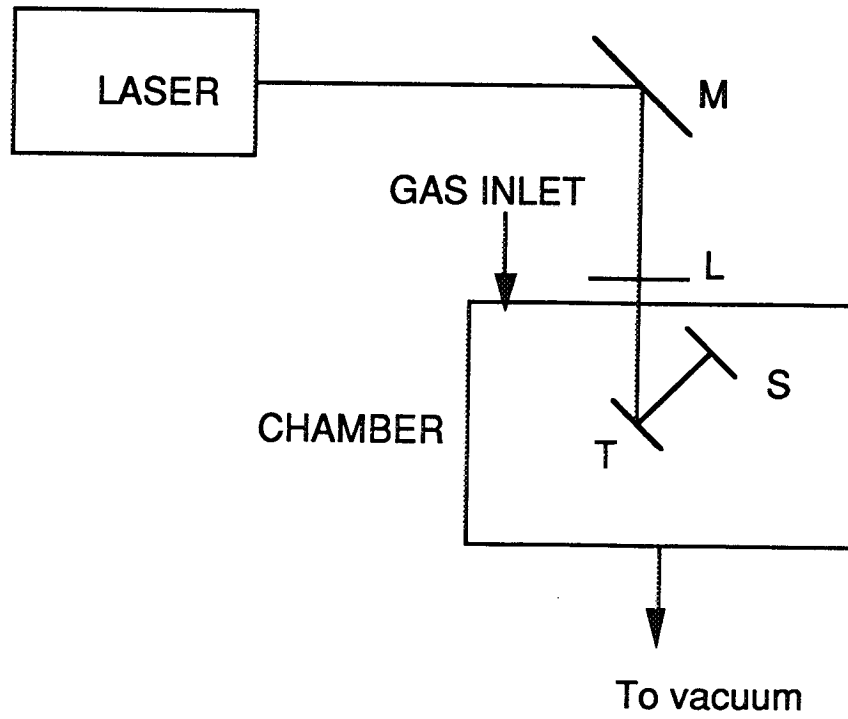
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Figure 2- Schematic of the PLD setup, where T is the target, S is the substrate material, M is the mirror, and L is the rotating focusing lens.
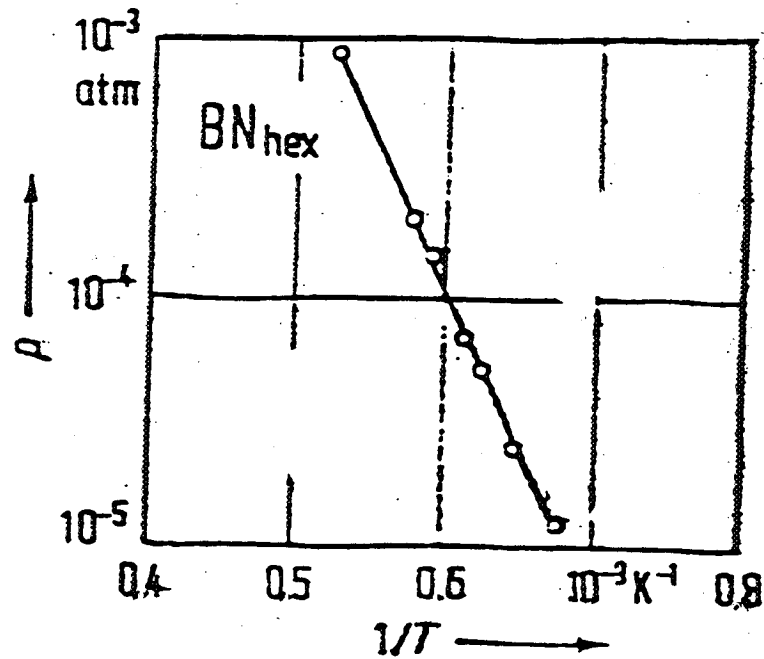

Figure 3- Pressure vs. (1/Temperature) plot for the formation of boron nitride [14].

The main advantage of the PLD scheme is that it is possible to deposit complex oxides [15]. Also, if there is a necessity to grow multilayers of films, it is possible to do so with the use of a polygon assembly. Here, the different materials to be deposited are loaded as target materials, and at the desired times, different targets are exposed to the laser beam. This technique might then be used to deposit complex layered oxides such as talc and pyrophyllite.

III. OBJECTIVE OF THIS PROJECT

The objective of this project was to attempt to design an inorganic water-repellent coating for thermal protection insulation on an aerospace vehicle. The candidate material of choice for experimentation was boron nitride. The substrate material used in our work was fused quartz. The deposited thin film was characterized by a variety of techniques, such as, X-ray diffraction, X-ray photo electron spectroscopy, and scanning electron microscopy.

IV. EXPERIMENTAL

The chemical vapor deposition (CVD) of boron nitride was conducted in collaboration with Professor R. Levy at the Department of Electrical Engineering and Computer Science, New Jersey Institute of Technology. The deposition scheme was the one currently used by their group [11]. The films were deposited in a low pressure CVD (LPCVD) reactor consisting of a fused silica tube having an inner diameter of 13.5 cm and a length of 144 cm. The chamber was mounted in a horizontal manner within a three-zone 10 kW tubular furnace. The vacuum conditions were achieved through a dual-stage rotary vane pump and a roots blower. The furnace temperature was maintained constant over the three zones of the reactor. The substrate material was fused quartz. The starting materials were triethylamine borane (liquid precursor) with nitrogen as the carrier gas, and ammonia. The temperature conditions within the reactor were greater than 800 °C and less than 1000 °C.

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The flow rate of triethlyamine borane was maintained at 17 sccm. The final film chemical composition was carbon, boron and nitrogen.

The pulsed laser deposition (PLD) was carried out at the Integrated Materials Laboratory at the University of California, Berkeley. The depositions were performed in the LEXTRA PLD system with KrF Excimer laser 248 nm radiation. The substrate material was fused quartz, and the substrate temperature was maintained at 600 °C. The pressure was maintained at 10^{-4} atm and the pressure inside the reactor was controlled with nitrogen gas. The laser density was 2 J cm^{-2}, the pulse time was 30 ns for the laser, and the number of shots that were fired were 15000. The target material used for this study was the cold-pressed boron nitride powder that we used for the thermal cycling study [6].

V. RESULTS

The deposited films were first characterized by X-ray diffraction, then with scanning electron microscopy, and finally by X-ray photoelectron spectroscopy.

X-ray Diffraction

The deposited films were analyzed with a X-ray diffractometer using copper-Kα radiation at operating conditions of 40 kV and 30 mA. The samples obtained by both CVD and PLD were found to be amorphous in nature. Broad diffuse peaks obtained in the intensity as a function two times the Bragg angle plots seemed to suggest our conclusion. Therefore, we did not do the rocking curve analysis around the diffraction peaks to study the orientation properties of the film.

SEM analysis

The microstructure of the thin films was analyzed using SEM. In the case of the CVD samples, the surface was found to be relatively smooth. This is in accord with the expected conformal coverage characteristics of the CVD process. However, with the PLD

samples, there were deposits of particles in the micron size range contributing to some amount of surface roughness. During the deposition process, high energy density is incident on the target material. This energy is capable of carrying some of the particles from the cold-compact pellet towards the substrate. Therefore, we attribute this to some particles actually being carried away from the target during the ablation process. The SEM micrographs for the CVD and PLD depositions are shown in Figures 4 and 5, respectively.

X-ray Photoelectron Spectroscopy

Using XPS we obtained the surface chemical composition. The elemental composition was obtained using magnesium $K\alpha$ radiation at operating conditions of 400 W, and the base pressure in the system was around 10^{-9} Torr. For the CVD samples, the composition was 34 % carbon, 40 % boron, 12 % nitrogen and 14 % oxygen. This was slightly different from the values reported by Levy' s group. The PLD samples contained boron at 41 %, nitrogen (24 %), oxygen (17 %), and carbon (18 %). The oxygen contamination in the films was mainly due to the residual oxygen content coming from the degassing of the walls of the reactor due to prior oxide depositions. For the PLD samples, after cleaning the surface with an argon beam, the carbon content was found to be completely absent, suggesting possible adsorption of organic contaminants (52 % B, 34 % N, 14 % O).

Contact Angle Measurements

The contact angle of a water droplet on the thin film samples was measured at room temperature by the sessile drop method, the same technique that was used in our initial project [6]. The contact angles obtained were close to 60 degrees, values that are identical to those obtained with the crystalline powder-pellet samples. This seems to suggest that for boron nitride, the contact angle is independent of the extents of crystallinity that may exist in the material, either in the form of a powder or in the form of a thin film.
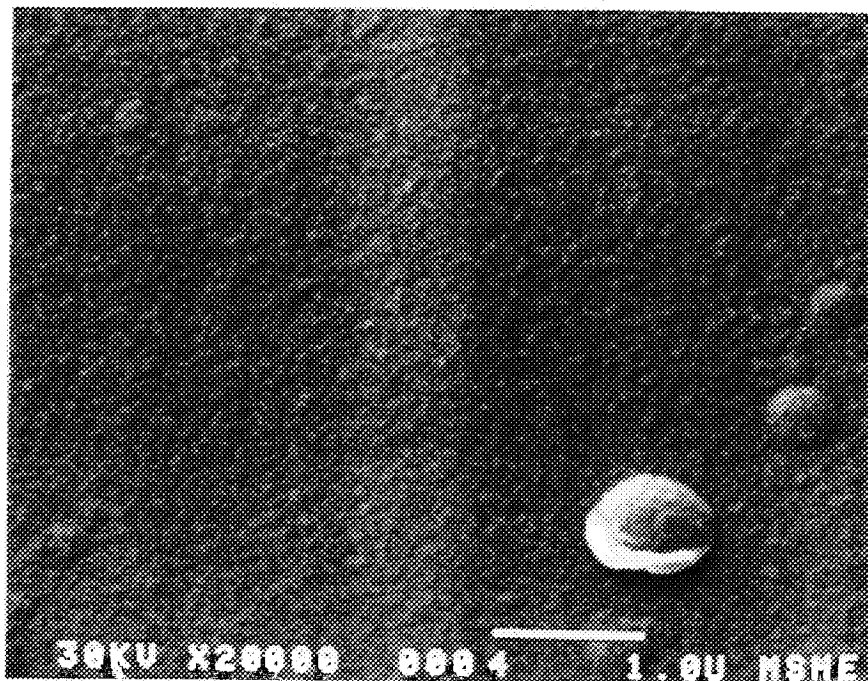
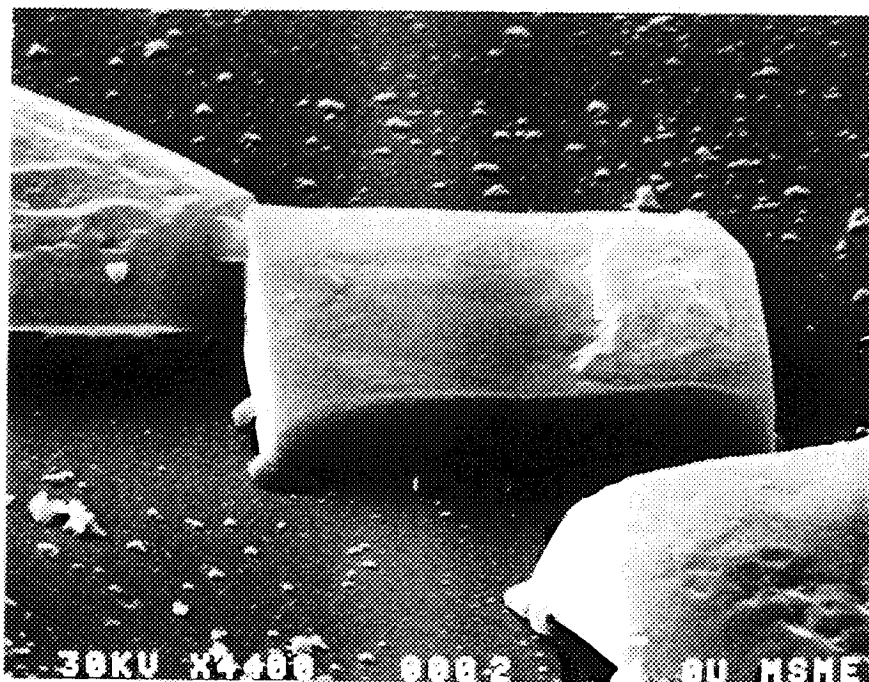Figure 4- SEM micrograph of boron nitride thin film deposited by CVD.

Figure 5- SEM micrograph of boron nitride thin film deposited by PLD.

VI. CONCLUSIONS

The deposited thin film of boron nitride on fused quartz exhibited identical contact angles to those measured with the cold pelletized samples. The films obtained with CVD and PLD were mainly amorphous in nature. The CVD films contained a large amount of carbon and boron nitride, the carbon being present due to the choice of the starting materials. With PLD, the films were found to rougher, probably due to the transport of loose particles from the target to the substrate.

The important finding is that the thin film of boron nitride exhibited similar contact angles/wetting behavior as had been observed with bulk pellet samples of the same material. This suggest the utility of screening the wetting behavior of candidate materials by using the wetting behavior of pellets as outlined in our first report [6]. Although not attempted here, thin film deposition techniques for complex oxides may be able to be carried out by pulsed laser deposition techniques, or possibly through the use of metal-organic precursors for CVD processing. Considerably more research would be required in the future to delineate the viability of using such techniques for producing suitable inorganic water-repellent coatings on silica-alumina fibers for TPS applications.

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