PROPERTIES OF CHEMICAL VAPOR INFILTRATION DIAMOND DEPOSITED IN A DIAMOND POWDER MATRIX

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ABSTRACT. Densifying non-mined diamond powder precursors with diamond produced by chemical vapor infiltration (CVI) is an attractive approach for forming thick diamond deposits that avoids many potential manufacturability problems associated with predominantly chemical vapor deposition (CVD) processes. We have developed two techniques: electrophoretic deposition and screen printing, to form nonmined diamond powder precursors on substrates. We then densify these precursors in a hot filament assisted reactor. Analysis indicates that a hot filament assisted chemical vapor infiltration process forms intergranular diamond deposits with properties that are to some degree different from predominantly hot-filament-assisted CVD material.

INTRODUCTION.

Chemical vapor deposited (CVD) diamond is currently the focus of numerous and diverse research, development, manufacturing and marketing activities. The combination of extraordinary properties that diamond displays, including (1) the highest thermal conductivity (above 300°K), (2) optical transparency from the near ultraviolet to the far infrared, (3) superlative hardness and (4) exceptional x-ray transmittance promise many unique applications.^{1,2} Certain potential applications for diamond, e. g. (1) thermal conductors for cooling dense electronic packages,

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(2) optical windows, and (3) strong, refractory, inert, low density material for load bearing structures require relatively thick diamond coatings or free-standing pieces.

At the present time, there are a number of problems associated with depositing thick, predominantly CVD diamond with properties approaching those of the best natural diamond. Diamond grown from a low pressure vapor phase may be flawed and twinned.³ Thick, predominantly CVD diamond typically possesses high levels of intrinsic stress which detracts from mechanical strength and stability.⁴ Simple, cost effective techniques for patterning diamond have not been widely developed. The surface roughness of predominantly CVD diamond characteristically increases with coating thickness. There is no simple, cost effective technique for smoothing or tailoring this rough surface topography.⁵ Typical growth rates are low, 1 to 10 μm per hour.⁶ The density of predominantly CVD diamond cannot be varied over a wide range.

In order to circumvent these and other potential problems associated with predominantly CVD material, we deposit non-mined diamond powder precursors, then densify these structures with chemical vapor infiltration (CVI) diamond. Below we discuss two techniques for depositing diamond powder precursors: (1) electrophoretic deposition and (2) screen printing a diamond paste. Representative properties of these deposits after densification with CVI diamond are described. This approach yields useful, novel and unique structures that are difficult or impossible to produce by chemical vapor deposition alone.

EXPERIMENTAL

A. Electrophoretic Deposition.

Useful, electrophoretically active, diamond particle baths can be prepared by mixing 0.5 to 2.5 wt.% nonmined diamond powder (from General Electric Corp., Diamond Products, Worthington, Ohio) with particle sizes below 3 μm in either deionized water, absolute ethanol or reagent grade isopropanol. Uniformity problems occur when water-based baths are used. Ethanol baths produce useful powder deposits, but ethanol is a controlled substance. For these reasons we elected to work primarily with isopropanol-based baths.

As-received nonmined diamond powder does not readily disperse in water, ethanol or isopropanol. When diamond is added to these liquids, it initially displays erratic electrophoretic activity. Sonicating these baths for approximately one hour (using a 40 kHz ultrasonic cleaner with sufficient power to heat the baths to temperatures from 40 to 70 °C) yields stable electrophoretically active dispersions with reproducible properties. These baths can be reused until practically all the diamond powder has been deposited onto substrates if they are periodically sonicated.

Diamond particles below approximately 1 μm in size deposit onto anodically biased substrates. Baths with particles from 2 to 3 μm contain both positive and negative charged particles. We generally used baths containing submicrometer-sized particles to deposit diamond onto a variety of positively-biased substrates including silicon wafers and commercial purity nickel sheet.

We typically operated using a fixed voltage of 1000 V across an electrodes spacing of 1 to 1.5 cm with electrolyte temperatures of 20 to 40 °C and deposition times of two minutes or less.

B. Screen Printing a Diamond Ink.

We prepared diamond inks containing mixtures of raw stock particle sizes ranging from 54 to 80 μm down to less than half-micrometer. We mixed diamond powder with a variety of organic liquids and gels including (1) reagent grade benzyl alcohol, (2) a gel containing approximately 30 wt. % N-22 ethyl cellulose (from Hercules Inc./Aqualon, Wilmington, DE) in reagent grade alpha-terpineol thinned with benzyl alcohol and (3) a proprietary thick-film vehicle, HTSC (from Zyp Coatings, Inc, Oak Ridge, TN). Some inks were prepared with a distribution of particle sizes that, in principle, yielded precursors with minimal porosity, i. e. 1 part by weight of a maximum particle size, plus 0.4 parts by weight of a powder with particle sizes approximately equal to 1/10 of the maximum particle size, plus 0.16 parts by weight of a powder with particle sizes approximately equal to 1/100 of the maximum particle size.⁷ Inks with a single distribution or a bimodal distribution of particle sizes that yield more porous precursors were used to investigate precursor porosity effects.

Approximately 1 part (by weight) powder was mixed with 1 part vehicle plus thinner to form a paste. The composition of this paste was adjusted empirically by adding small amounts of powder or liquid to obtain thixotropic flow characteristics appropriate for screen printing. This paste was then squeegeed through patterned openings on 150 μm (0.006 inch) or 300 μm (0.012 inch) thick masks onto silicon or nickel substrates. The wet deposits were air dried at 70 to 90 °C. When vehicles with binders were used, the binder in these preparations was driven off by heating the powder precursors to 450 or 500 °C at 10^{-6} Torr for 1 hr in the CVD/CVI reactor immediately before commencing CVI densification.

A number of extremely thick deposits were formed by iteratively printing a 200 μm thick bimodal $\leftarrow$ powder deposit (after shrinkage from a 300 μm mask) then densifying, then repeating the printing and densification process.

C. Chemical Vapor Infiltration.

The powder precursors were densified in a hot filament assisted CVD/CVI reactor. A small area on silicon substrates adjacent to the precursors was abraded with diamond grit then wiped "clean" with a isopropanol soaked swab to initiate the deposition of predominantly CVD diamond, so that the properties of CVD diamond could be compared to the properties of the CVI material deposited in the same run. The reactor was equipped with a rhenium filament, spaced 1.5 cm from the substrates at closest approach. The filament was operated at temperatures from 2100 to 2300 °C, confirmed with a two-color optical pyrometer. A 2.5 cm diameter, resistively heated platform with a thermocouple heated substrates to temperatures from 600 to 950 °C. The effects of using 10 to 20 Torr reactive gas mixtures containing from 0.5 to 2 % ultra high purity CH₄ plus ultra high purity hydrogen were explored. Process times extended from 4 to 24 hours.

RESULTS AND DISCUSSION

A. Electrophoretic Deposition.

The water-based electrophoretic baths produced rough, irregular, poor quality coatings (Figure 1a). Coating roughness is, in part, due to the relatively low voltage required to dissociate water into oxygen and hydrogen that results in oxygen bubbling over the substrate. Macroscopic coating topography suggests that flocs form, then deposit onto the substrate, inferring that non-mined diamond powder is somewhat hydrophobic. Relatively smooth, uniform, conformal diamond powder coatings can be electrophoretically deposited from ethanol and isopropanol baths (Figure 1b). Threshold voltages of 20 to 50 V across 1 to 1.5 cm

yield visible deposits after approximately 5 to 30 sec depending on bath concentration. More concentrated baths draw higher current densities and yield faster deposition rates at a given voltage. Nominal coating thicknesses approaching 50 μm (calculated from weight gain and diamond density) can be electrophoretically deposited in 1 min from a 2.5 wt. % diamond powder plus isopropanol bath operated at a cell voltage of 1000 V across an electrode spacing of 1.5 cm.

The powder particles in these coatings are held together by hook-and-claw adhesion and Van der Waal's forces. Problems occur when the coatings reach a certain thickness and lack sufficient cohesive strength to support their own weight. Stronger coatings form at relatively high electric field strengths, e. g. 1000 V cell voltage across an electrode spacing of 1.5 cm, in high concentration baths (with 2.5 wt. % diamond). Increasing the distribution of particle sizes in the bath serves to increase coating density and cohesive strength, and reduce shrinkage and cracking.

Dispersions with more than 2.5 wt. % diamond tend to be unstable. Hard aggregates that cannot be ultrasonically fractured and redispersed form during extended storage. The particles in high concentration baths, especially in conjunction with high electric field strengths, tend to floc in the vicinity of the substrate; the density of these flocs causes them to sink before they contact and adhere to the substrate, resulting in partial or no net coating deposition.

Diamond particles tend to deposit first on high field areas , e. g. exterior corners. These initial deposits tend to screen subsequent deposition in these areas and low field areas become coated. Conformal coatings form on shaped substrate after a certain amount of processing time (Figure 1c).

Useful diamond powder coatings thicker than approximately 200 to 250 μm (Figure 1d) cannot be electrophoretically deposited for several reasons: (1) The minimum threshold field strength required for deposition and floc formation at high field areas in combination with (2) an increased probability of dielectric flaws with continued deposition, (3) the limited coating weight defined by cohesive strength, and (4) the shrinkage and cracking that occur when the coatings dry all contribute to define maximum useful powder coating thickness.

In summary, attributes associated with electrophoretic deposition of diamond powder precursors include (1) processing speed, simplicity and cost effectiveness, (2) ability to form conformal coatings readily on shaped substrates and (3) opportunities for controlling coating thickness by controlling cell voltage, bath concentration, and deposition time. Potential problems and complications may arise based on a number of considerations: (1) Substrates must be electrically conductive. (2) Precursor surface smoothness begins to suffer when coatings thicker than 100 μm are formed. (3) Useful precursors thicker than 200 to 250 μm cannot be formed. (4) Opportunities for varying coating porosity (to expedite CVD or form tailored structures) are limited. (5) The dried powder deposits are soft and fragile, which curtails subsequent options for mechanically smoothing or shaping surface topography.

B. Screen Printing Diamond Powder Inks.

Many potential problems and limitations associated with electrophoretically deposition can be avoided by screen printing or painting a diamond powder containing ink or paste. Inks generally contain powder dispersed in a liquid vehicle which may include dissolved material

that acts as a binder after the ink dries. The rheological properties of an ink are critically important in any printing or painting operation. The rheological properties of an ink depend on vehicle composition, concentration and particle size. Our immediate objectives were (1) to demonstrate that diamond powder inks with a large variety of particle sizes conducive to a wide variety of powder precursor porosities could be deposited onto substrates and densified in a CVD/CVI diamond reactor and (2) to demonstrate that the processes of printing and densification could be repeated to iteratively build thick diamond deposits. Developing specific formulations for high resolution printing is beyond the scope of this study.

Inks which contain submicrometer particles yield low porosity precursors. Benzyl alcohol is an essential ingredient in preparations containing submicrometer-sized diamond particles. Benzyl alcohol appears to wet fine diamond powder and inhibit aggregation. Proprietary thinners such as DuPont 7480, the proprietary Zyp Inc. vehicle and the generic ethyl cellulose plus alpha terpineol preparations with no added benzyl alcohol allow ultrafine diamond particles to aggregate.

In addition to inhibiting aggregation, benzyl alcohol is a desirable liquid for adjusting ink viscosity because it evaporates slowly at room temperature, producing ink with a long "pot life". Unfortunately, the rheological properties of these simple benzyl alcohol plus diamond powder inks leave much to be desired with regard to pattern resolution. After drying, these precursors are soft and do not adhere strongly to substrates. Softness and poor adhesion limit opportunities for mechanically tailoring the powder precursors before densification.

A diamond ink with benzyl alcohol, plus the generic or the proprietary vehicle is superior to ink prepared simply from diamond powder plus

benzyl alcohol. Dry powder precursors prepared using the generic or proprietary vehicles are sufficiently robust to survive mechanical contouring, smoothing or thinning after drying. Additional powder layers can be printed directly on these strong, dry deposits. The multicomponent formulations display improved rheological properties compatible with improved pattern resolution. Printing and painting techniques are suitable for forming diamond precursors that exceed 100 μm in thickness with tailored porosities and surface topographies on selected areas. The degree and rate of CVI densification depend on the porosity and thickness of the powder precursor. If extremely thick dense deposits are required, they can be built up iteratively, by printing powder then densifying, and repeating these two basic steps until the desired thickness and density are achieved.

coating quality and working gas composition is typically observed by groups depositing hot filament assisted or microwave plasma assisted CVD diamond.⁸ The diamond Raman band is most dominant for CVI material formed at lower substrate temperatures (700 °C) as compared to the substrate temperatures where many groups report repeatably observing their best quality CVD material (850 to 900 °C) for methane plus hydrogen gas chemistries.⁸ The Raman spectrum of predominantly CVD diamond deposited on diamond-seeded 700 °C substrates in our reactor is similar to the spectrum of the 700 °C CVI material represented by Fig. 3a. However when marginal conditions for diamond deposition are present in our reactor, the composite material contains a higher concentration of sp^3 diamond bonds than the CVD material (compare Fig. 3b to 3c). Fluorescence data indicate the CVI material contains trace amounts of silicon and boron from boron doped silicon wafer substrates. Silicon and boron are not present in diamond composites formed on nickel substrates. With the exception of fluorescence due to silicon and boron, the Raman shifts exhibited by freestanding composites removed from nickel substrates are similar to those displayed by composite coatings formed on silicon.

Transmission electron microscopy indicates the CVI diamond replicates and enlarges interior diamond particles (Figure 4 a and b). Diffraction patterns indicate the diamond composite material contains relatively few defects and little twinning (Figure 4c). Plan view scanning electron micrographs of densified composites show a faceted topography with predominantly triangular (111) surface planes (Figure 4d). Larger surface grains form on composites densified at higher substrate temperatures. The surface morphology of the composites is very similar to the surface morphology found on predominantly CVD material. This suggests that

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during the densification process the porous precursor was sealed by a CVD skin. Thin buried CVD skins can be detected in extremely thick deposits formed by iteratively printing diamond ink then densifying (see Fig. 2b). The presence of these skins indicates that additional process refinement in conjunction with porosimetry measurements is necessary to optimize this approach.

SUMMARY AND CONCLUSIONS.

We have demonstrated that it is possible to form thick, relatively stress free, diamond coatings in relatively short amounts of time by first electrophoretically depositing or screen printing a porous diamond powder coating, then filling in the pores with hot filament assisted CVI diamond. Stronger composites form from denser green ceramic diamond powder precursors. When silicon is used as a substrate material, extensively densified composites adhere strongly to the substrate. When nickel is used as a substrate, strong freestanding pieces of diamond can be removed from the substrate after densification. Except for substrate adhesion and the presence of trace amounts of boron and silicon in composites formed on silicon, there are no major differences between composites formed on nickel or silicon substrates determined by Raman spectroscopy. Raman spectroscopy indicate the best quality diamond composites form at substrate temperatures of 700 °C in 0.5 % methane plus hydrogen. When reactor conditions are not optimal, the composite material contains higher concentrations of ² diamond than predominantly CVD material. Transmission electron microscopy indicates envelopes of CVI diamond are forming around diamond particles within the precursors. Electron diffraction patterns show this CVI material is relatively free of flaws and twinning. Scanning electron micrographs of densified composite surfaces show an apparently continuous skin of faceted diamond growth similar to the surface topographies observed by groups evaluating predominantly CVD diamond growth processes. The presence of this surplus CVD skin indicates future parameter refinements are required to optimize this CVI diamond densification process.

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REFERENCES

1. R. M. Chrenko and H. M. Strong, Physical Properties of Diamond, Technical Report No. 75CRD089, Oct. 1975, General Electric Company, Corporate Research and Development, Schenectady, N. Y.
2. K. E. Spear, J. Am. Ceram. Soc. 72, 171 (1989).
3. C. V. Cooper and C. Beetz, Jr., Surface and Coatings Technology, 47, 375 (1991).
4. S. Jin, J. E. Graebner, M. McCormack, T. H. Tiefel, A. Katz and W. C. Dautremont-Smith, Nature, 362, 822 (1993).
5. P. R. Chalker, A. M. Jones, C. Johnson and I. M. Buckley-Golder, Surface and Coatings Technology, 47, 365 (1991).
6. Stephen J. Harris and Anita M. Weiner, J. Appl. Phys. 70, 1385 (1991).
7. W. D. Kingery, Introduction to Ceramics, John Wiley and Sons, Inc. New York, (1967) p 34.
8. D. M. Tung, W. L. Hsu, and K. F. McCarty, "Characteristics of Diamond Films Deposited in a Microwave Plasma", Proceedings of the 1st International Symposium on Diamond and Diamond-Like Films at the 175th Meeting of the Electrochemical Society, Los Angeles CA, May 7

-12, 1989, ed. J. P. Dismukes et al., Vol 89-12, pub. Electrochemical Society, Inc., Pennington, NJ, p 500.

FIGURE CAPTIONS

Figure 1. Electrophoretically deposited 0 to 0.5 μm nonmined diamond powder. A. Reniform clusters from an aqueous bath. B. A relatively uniform deposit from an isopropanol bath. C. A deposit on a shaped substrate (a steel carriage bolt). D. A 250 μm nominal thickness deposit from an isopropanol bath.

Figure 2. Densified, screen printed precursors. A. An extremely thick, 625 μm deposit. B. Higher magnification view showing a buried CVI/CVD skin. C. Plan view of a partially densified powder deposit with faceted CVD diamond growth on surface diamond particles.

Figure 3. Raman spectra shifts. A. and B. From CVI densified screen printed diamond powder precursors processed at A. 700 ° C and B. 900 °C CVI substrate temperatures. C. Predominantly CVD material formed at 900 °C. (The 600 cm^{-1} shift is silicon substrate shine-through from this relatively thin deposit.)

Figure 4. TEM and SEM analysis of CVI diamond deposits. A. Initial stage of densification. CVI material envelopes a diamond particle. B. As densification progresses, a thicker deposit grows around a particle. C. Electron diffraction pattern showing densified material has a well developed diamond structure. D. SEM plan view showing a faceted CVD diamond surface topography .

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