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Growth of cubic boron nitride on diamond particles by microwave plasma enhanced chemical vapor deposition

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The nucleation and growth of cubic boron nitride (*c*-BN) onto diamond powder using solid $NaBH_4$ in low pressure gas mixtures of NH_3 and H_2 by microwave plasma enhanced chemical vapor deposition has been studied. Boron nitride was deposited on submicron diamond seed crystals scattered on (100) silicon single crystal wafers and evidence was found for the formation of the cubic phase. Diamond powder surfaces appear to preferentially nucleate *c*-BN. In addition it was found that the ratio of *c*-BN to turbostratic structure boron nitride (*t*-BN) deposited increases with decreasing NH_3 concentration in H_2. It is suggested that this may be due to an increased etching rate for *t*-BN by atomic hydrogen whose partial pressure may vary with NH_3 concentration.

Cubic boron nitride (*c*-BN) is of great interest for numerous reasons and among these is its potential, along with diamond and SiC, as a high temperature semiconductor. Cubic BN has a large band gap,[1–3] and doping to achieve both *p*- and *n*-type behavior has been demonstrated using high pressure and high temperature methods.[4] In addition rectifying diode characteristics have been measured on rudimentary junctions prepared using *c*-BN[5] and in this sense progress with *c*-BN can be thought of as more advanced than the work in diamond. However research with *c*-BN has seriously lagged progress with SiC or diamond in one critically important area and that is that there is not yet a suitable vapor phase [e.g., low pressure chemical vapor deposition (CVD)] method for the steady state growth of well crystallized material. Experiments with both physical and chemical vapor deposition (PVD and CVD) techniques appear to have produced some cubic material but this is of low quality with very limited crystallite size and perfection, much too poor to be useful for electronic devices. Although the heteroepitaxial growth of *c*-BN onto silicon has been claimed,[6] the lattice parameter reported for this material is substantially larger than that for the stoichiometric material prepared by high pressure methods. Growth rates are limited and hydrogen (atomic and possibly molecular) can act as a selective etching agent and lead to a loss of stoichiometry through such reactions as

$$BN_{(s)} + 3H^0 \rightarrow B_{(s)} + NH_3, \qquad (1)$$

where the subscript *s* denotes a solid. Such reactions may introduce a complication not present in the CVD of diamond. Typical crystal sizes reported are 50 nm by microwave plasma enhanced CVD[7] and hot filament assisted rf plasma CVD,[8] and 10 to 20 nm by electron cyclotron resonance (ECR) plasma CVD.[9] Polycrystalline films, <1 μm in thickness, have been formed using PVD methods such as arc-like plasma enhanced ion plating,[10] by sputtering of boron nitride targets,[11] and most recently, by magnetically enhanced, radio frequency (rf) plasma methods.[12]

To achieve material suitable for many applications, including electronic devices, not only is stable steady state growth important, but also an understanding of nucleation. Scratching of silicon substrates by diamond powder has been shown to increase the density of nucleation in the CVD of diamond[13,14] and it has been shown that the epitaxial growth of diamond films occurs on (100) and (110) single crystal diamond.[15,16] In addition diamond has been grown very efficiently and heteroepitaxially on both large crystals and fine powders of high pressure synthesized cubic boron nitride.[14,17,18]

We have reported the preparation of nanocrystalline *c*-BN with $NaBH_4 + NH_3 + H_2$ by microwave plasma enhanced CVD[7] and a diagram of the experimental arrangement for this work can be seen in Fig. 1. Using this method, the deposition rate for a hard amorphous phase was greater than that of the cubic phase. It is shown here that an amorphous phase is also formed on diamond powder under the same experimental conditions. In this study, the distance between the solid boron source, $NaBH_4$, and the substrate was increased from 10 to 20 mm in order to reduce the local concentration of gas phase species and hence the deposition rate. With these conditions and in the absence of diamond powder, only small amounts of an amorphous phase were seen on an untreated silicon substrate in three hours of deposition. In addition the observed intensity of IR absorption at 1080 cm^{-1} (attributed to the F_2 vibrational mode of *c*-BN) using FTIR was significantly less than in samples prepared with shorter distances between the solid boron source and the substrate. After scattering natural diamond powder (<1 μm) on the silicon wafers, BN films were deposited showing a much stronger IR absorbance at 1080 cm^{-1}, suggesting that the presence of natural diamond powder, which does not absorb, has increased the yield of sp^3 hybridized material.

Figure 2 shows the FTIR absorption spectra for BN films deposited for 3 h at various NH_3 concentrations in H_2. The gas pressure and total gas flow were kept constant at 100 Torr and 20 sccm, respectively. The sodium borohydride, $NaBH_4$, 50 mg, was held in a BN crucible below the substrate. The substrate temperature was 1000 °C, and was measured using a single wavelength optical pyrometer at 650 nm without an emissivity correction. The absorption at 1080 cm^{-1} is attributed to the F_2 vibrational mode of *c*-BN. The absorptions at 1380 and 805 cm^{-1} are attrib-

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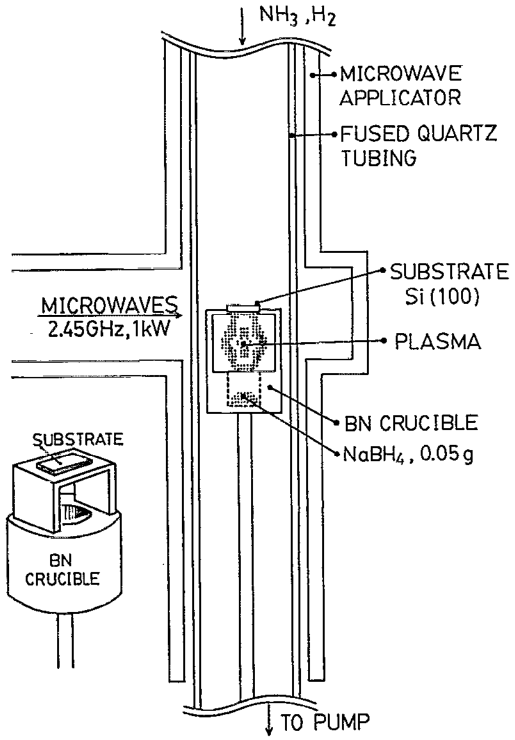

FIG. 1. Schematic diagram of the microwave plasma enhanced CVD reactor.

utable to the in-plane vibrational modes of pyrolytic BN (*h*-BN) and/or a turbostratic structure BN (*t*-BN). Results from TEM study suggest that the material is turbostratic, i.e., that it lacks long range order along the *c* axis. The small absorption seen at ~910 cm^{-1} is not presently understood. Although, the relative absorption intensity for *c*-BN was increased by scattering of diamond particles on silicon substrates, the total deposition rate appeared lower than in previous experiments, giving rise to the suggestion that diamond powder surfaces may preferentially nucleate *c*-BN, similarly to the ready nucleation of diamond on *c*-BN surfaces.

The deposited films show electron diffraction patterns from diamond, *c*-BN and *t*-BN. Since the lattice mismatch between diamond and *c*-BN is only ~1.4%, it is difficult to clearly distinguish between these phases by selected area diffraction. However diamond shows only a very weak (002) diffraction, as this diffraction line is forbidden for the diamond structure and its presence in many specimens is believed due to crystal defects.[19] In contrast, *c*-BN shows a strong (002) diffraction. For examination by TEM, the coated silicon substrates were cut or fractured to approximately 1×3 mm pieces. This gave pieces on which portions of the film extended beyond the edge of the silicon substrate. A typical TEM image and electron diffraction pattern from a region of the deposited material, designated C$_2$, is shown in Fig. 3. In bright field examination, three different types of crystalline material can be discerned. The large thick crystals, designated C$_1$ (~1 μm in diameter) are diamond single crystals. Both the diffraction patterns and particle sizes observed are consistent with the diamond

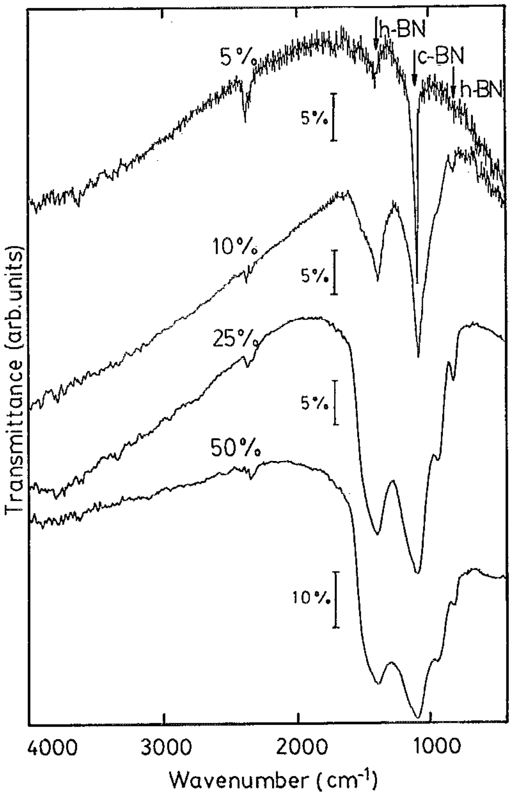

FIG. 2. FTIR absorption spectra of BN films deposited at various NH$_3$ concentrations in H$_2$ (C_{NH_3}) ranging 5%–50%. Bars show % transmittance.

powder used. The region designated C$_2$ consists of many small crystals that grew between the diamond particles. The diffraction patterns observed in this region indexed as a zinc blende structure with a lattice constant of $a_0 = 0.36$ nm, corresponding to *c*-BN and it is concluded that *c*-BN formed between diamond particles. In addition it appears that the crystals, 50–100 nm in size, designated as C$_3$ and similarly indexed as *c*-BN, grew from the surfaces of the diamond powder. Also it was found that when the amounts of diamond powder used were small, so that diamond particles were widely scattered, giving relatively few sites for nucleation, uniform films of *t*-BN were deposited. This implies that the relative yield of cubic material is dependent

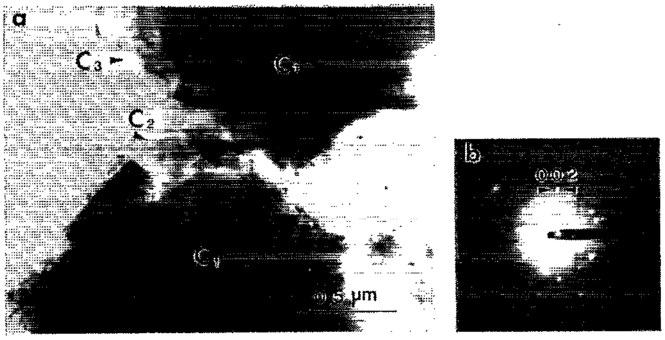

FIG. 3. (a) Typical TEM bright image of the film deposited at 25% in C_{NH_3}, and (b) electron diffraction pattern from region C$_2$.

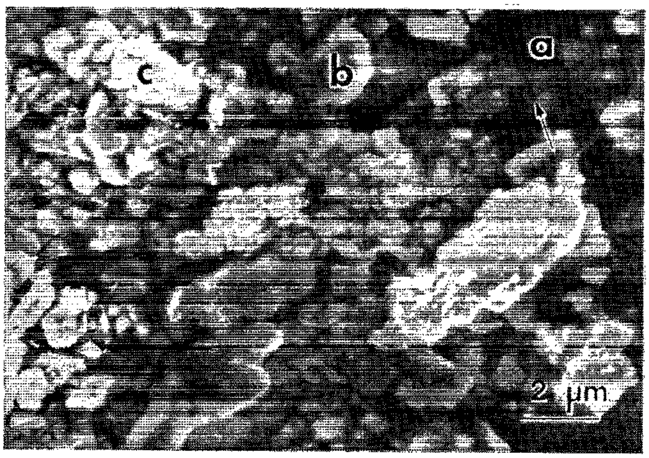

FIG. 4. Typical SEM micrograph of surface film deposited at 25% in C_{NH_3}.

on the amount of diamond present, giving further evidence that diamond surfaces preferentially nucleate cubic BN.

From SEM observations, BN forming between diamond particles was recognized. A typical example of the surface morphology of BN films deposited on diamond powder is shown in Fig. 4. Diamond particles in region (a) are completely enclosed by the deposited BN. This BN film is hard and displays evidence of surface microcracking, as indicated by the arrow, suggesting the presence of substantial residual stress. In earlier stages of film formation, BN grew between the diamond particles as shown in region (b) in Fig. 4. This is the same area of the sample as was used for the TEM bright field image shown in Fig. 3(a). No deposition was observed in several places on some of the diamond powder, seen in region (c) in Fig. 4, suggesting that gasification and redeposition of carbon alone are not a reasonable rationalization of these results. Since these deposits showed a uniform morphology, without obvious evidence of habit, regions of *c*-BN or *t*-BN could not be distinguished by SEM.

In Fig. 2, peak positions of FTIR absorption of *c*-BN and *t*-BN appear insensitive to deposition stoichiometry, however, their integrated absorption intensities ($S_{c\text{-BN}}$ for absorption at 1080 cm^{-1} and $S_{t\text{-BN}}$ for absorption at 1380 cm^{-1}) do change with increasing NH_3 concentration (C_{NH_3}). Figure 5 shows $S_{c\text{-BN}}$ and $S_{t\text{-BN}}$, and the absorption ration $[S_{c\text{-BN}}/(S_{c\text{-BN}} + S_{t\text{-BN}})]$ as a function of C_{NH_3}. As the C_{NH_3} is increased, the absorption ratio decreases to a constant of ~ 0.6. At C_{NH_3} greater than 10% the deposition ratio changes very little. Below 10% NH_3 the change in deposition ratio is significant. The change in the apparent ratio of *c*-BN to *t*-BN can be rationalized by a preferential chemical etching of *t*-BN by atomic hydrogen.[20]

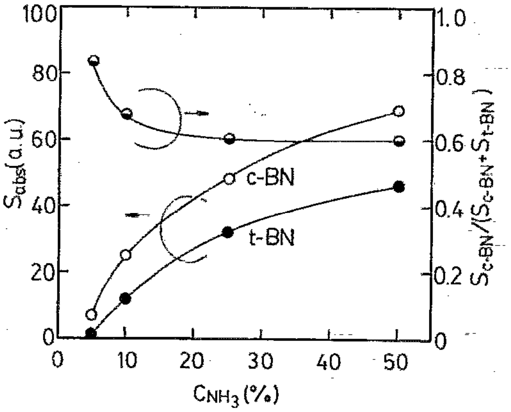

FIG. 5. Integrated infrared absorption intensity of *c*-BN ($S_{c\text{-BN}}$) and *t*-BN ($S_{t\text{-BN}}$), and intensity ratio $[S_{c\text{-BN}}/(S_{c\text{-BN}} + S_{t\text{-BN}})]$ as a function of C_{NH_3}.

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