A gas phase chemical etchant for boron nitride films

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A gas phase chemical etchant for boron nitride films

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We have demonstrated that boron nitride films deposited on silicon and tantalum can be etched in a hot filament environment with an input gas composition of 1% methane in hydrogen. Etching experiments were carried out at around 800 K on a tantalum foil and at somewhat higher temperatures on silicon substrates. If the etchant is atomic hydrogen or methyl radical, then we estimate etching efficiencies (atoms etched per collision) of $\sim 10^{-5}$ or 10^{-4} for these species, respectively. © *1995 American Institute of Physics.*

Boron nitride crystallizes into at least four known phases: hexagonal, rhombohedral, wurtzitic, and cubic. The former two phases are sp^2-bonded, while the latter are sp^3-bonded. The cubic phase of boron nitride (cBN) has many physical properties in common with diamond, such as extreme hardness, excellent thermal conductivity, and a wide band gap. Because of these and other properties, there have been many efforts to grow cBN films and coatings. Plasma enhanced CVD methods were employed to grow cBN due to their success in growing diamond films. However, it was soon observed that very little cBN could be grown by those methods. Attention soon turned to PVD processes, where there was greater success.[1] Even here, however, a substantial fraction of hexagonal BN has often been found.

That films meant to be pure cBN contain hexagonal or turbostratic BN seems understandable if hBN is more stable than cBN. However, the fact that graphite is more stable than diamond does not prevent high purity diamond from being grown. Diamond is nearly always grown with very high concentrations of atomic hydrogen, and the purest diamond is often grown with traces of oxygen. These species etch nondiamond (sp^2) carbon more readily than diamond, so that even if both diamond and nondiamond carbon are formed, only the diamond survives. Yarbrough[2] has speculated that one reason for the relatively low cBN fraction in films deposited by CVD is that no sp^2 etchant is present during its growth. There are little data available on etching of BN, although liquid phase etchants are known,[3] and ion,[4] and sputter[6] etching have been observed. In this work, we report the first experimental data demonstrating gas phase chemical etching of BN films.

BN films roughly 100 nm thick were deposited on 25 mm diam, 0.25 mm thick silicon wafers and on tantalum foil using the laser ablation technique.[6] After deposition the silicon wafers were broken into several pieces, and FTIR spectra were taken in transmission through each of them. Etching took place in a chamber made from a stainless-steel cross which could be evacuated with a mechanical pump or fed with either pure H_2 or with a 1% CH_4/99% H_2 mixture at 100 sccm and 18 Torr. From the measured leak rate, the oxygen concentration at the wafer is estimated at less than 10 ppm at 18 Torr. The BN-coated substrate rested on a 1 in. diam support which could be electrically heated. The support was moved with an *x-y-z* translation stage so that the substrate was 3 mm below a 250 μm diam carburized tungsten filament. The substrates were heated either by raising the temperature of the support to 1150 K or by raising the temperature of the filament to 2400 K (in which case the support was not electrically heated). In the latter case, the environment is identical to that for filament-assisted diamond film growth. Since diamond films grow in this environment only if the substrate temperature is between ~900 and 1400 K,[7] the presence of a diamond film on the substrate would indicate that the local temperature was in that range. We also measured the substrate temperature directly with a Pt/Pt–Rh thermocouple buried in and then expoxied to a surrogate silicon wafer. However, this wafer was 0.5 mm thick. The temperature of the tantalum foil during etching was measured with a Pt/Pt–Rh thermocouple which had been spot-welded on before BN film deposition. Etching experiments lasted for 30 min, after which the substrate was removed for examination by transmission FTIR in the case of the silicon substrate or by electron probe analysis[8] in the case of the tantalum foil.

Figure 1 shows a photograph of a BN-coated substrate before the etching treatment. Its FTIR spectrum is shown in Fig. 2. Features at 1380 and 780 cm^{-1} indicate that the film is sp^2-bonded BN, while smaller features at 1100 and 980 cm^{-1} are assigned to silicon oxides present on the uncoated side of the substrate. We performed four experiments with the silicon substrates to study the etching process. (1) A coated substrate was heated in vacuum with the support heater at 1150 K. After 30 min the substrate was removed for examination. Neither its visual appearance nor its IR spec-

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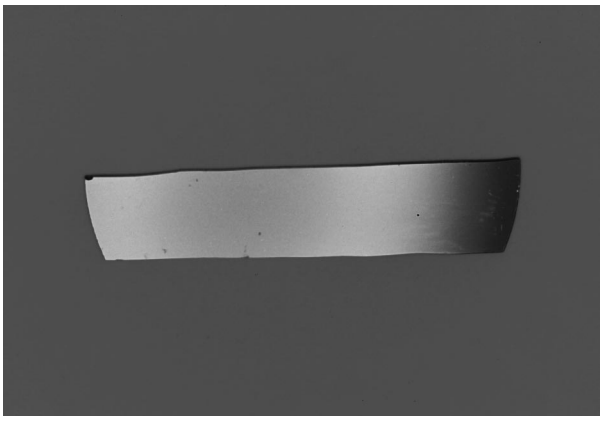

FIG. 1. BN film on 2.5 cm long silicon wafer before etching. The shading variations are due to variations in film thickness.

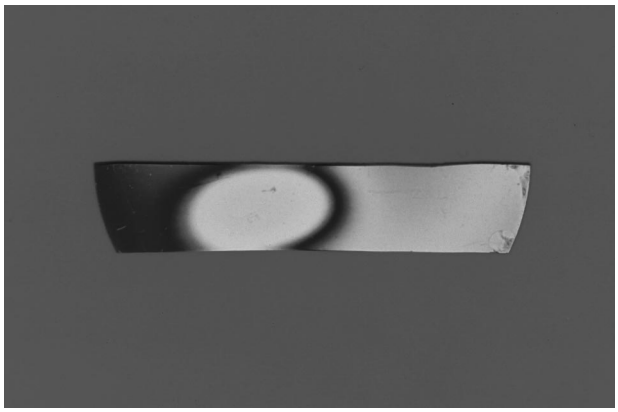

FIG. 3. BN film after etching. The oval region is the etched area, which was directly under the filament. It appears silver-colored, similar to bare silicon.

trum had changed significantly from what is shown in Figs. 1 and 2. This result demonstrates that the film does not evaporate, change chemical form, or dissolve in the substrate at this temperature. (2) A coated substrate was placed in the chamber with the support heated to 1150 K and with the 1% CH_4/99% H_2 mixture flowing at a pressure of 18 Torr for 30 min. Once again neither its visual appearance nor its IR spectrum was significantly affected. This result demonstrates that the film is not etched by CH_4 or H_2. (3) A substrate was placed in the chamber with the heater off but with the filament at 2400 K and with the 1% CH_4/99% H_2 mixture flowing at a pressure of 18 Torr. After 30 min the substrate, shown in Fig. 3, had a large etched area directly below the filament. An IR spectrum through the etched region (Fig. 4), indicates that the sp^2 BN absorption peak intensities were reduced by about 90%, while the silicon oxide absorption line intensities remained essentially unchanged. We therefore conclude that sp^2-bonded BN is etched by a species which is created by the hot filament. Etching was also observed for the film on the tantalum foil under these conditions as shown by an x-ray line profile taken on the foil with the electron probe. Based on the concentrations determined from our previous work with filament-assisted diamond CVD systems,[9,10] we judge that the most likely etchant candidates are atomic hydrogen (H) and/or methyl radical (CH_3) because these are the two most abundant free radicals in the gas phase. (4) This experiment was identical to (3) except that the gas was pure H_2. In this case, no etching was observed on the silicon substrate. This result could indicate that some carbon-containing species is necessary for etching. We note, however, that without CH_4 present the filament does not remain carburized, and tungsten may evaporate and coat the substrate.[11] It is possible that tungsten could protect the BN film from being etched.

Because filament heating is spatially inhomogeneous and the thermal conductivity of silicon is relatively low, the substrate temperature could vary considerably from position to position. The surrogate silicon wafer with the thermocouple attached indicated that the substrate temperature in the etched region was between 750 and 1000 K. However, this wafer was twice as thick as the one on which we grew and etched the BN film. In a separate experiment, we found that under the conditions of experiment (3) a diamond film grew on a clean silicon substrate which had been polished with diamond paste, as shown in Fig. 5. A comparison of Figs. 3 and 5, which are shown to the same scale, indicates that diamond growth could have been supported everywhere in the etched region, which means that the temperature in the etched region on silicon must have been between 900 and 1400 K. The maximum temperature of the tantalum foil was

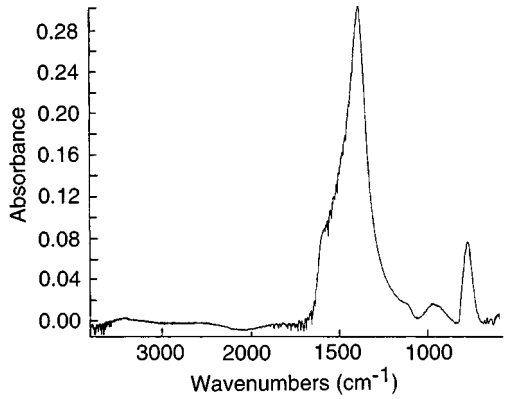

FIG. 2. FTIR spectrum taken in transmission of the film shown in Fig. 1. The larger features at 1380 and 780 cm^{-1} are from BN. The smaller features near 1000 cm^{-1} are from silicon oxides on the backside of the wafer.

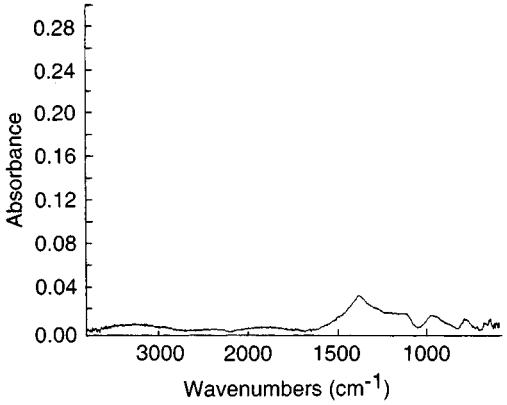

FIG. 4. FTIR spectrum taken in the etched region shown in Fig. 3. Features due to BN are reduced by ~90%.

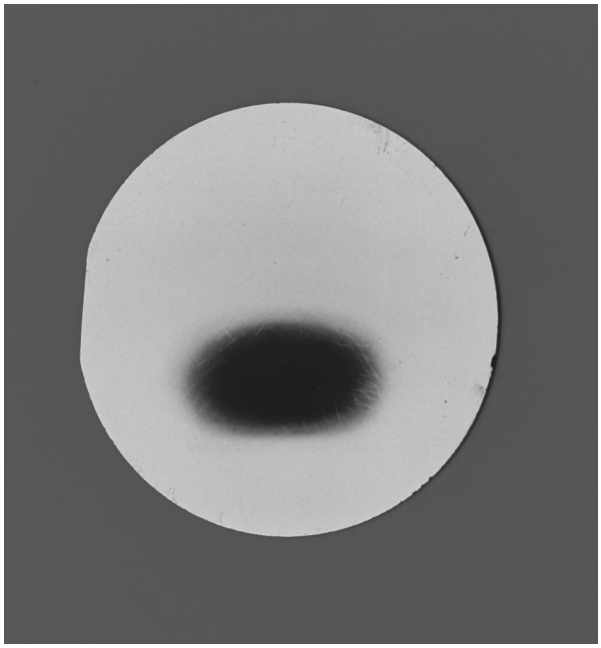

FIG. 5. 2.5 cm diam silicon wafer. The dark oval is a diamond film. Its dimensions are slightly larger than the etched region shown in Fig. 3.

lower (about 800 K), as expected due to its high thermal conductivity relative to silicon.

Because the diamond growth region was larger than the etched region (compare Figs. 3 and 5), the temperature just outside the etched region must have been at least 900 K; i.e., 100 K hotter than in the etched region on the tantalum foil. The fact that no etching took place in this region of the silicon wafer indicates that the etching boundary was determined by the gas phase composition above the surface rather than just by substrate temperature. Harris and Weiner[12] and others[13] have measured H and CH_3 concentrations in similar hot filament environments, and based on these measurements and the observed etch rate we estimate an etching efficiency of roughly 10^{-5} atoms etched per H collision, or 10^{-4} atoms etched per CH_3 collision, if these species are the etchants.

Future work will involve determination of gas phase species concentration profiles as well as the relative etching rates of the various phases of boron nitride.

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