

Diamondlike properties in a single phase carbon nitride solid

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The intrinsic properties and bonding of single phase carbon nitride thin films of stoichiometry C_2N have been studied. C_2N exhibits high electrical resistivity and thermal conductivity that are similar to the properties shown by diamondlike carbon (DLC) films. Electron energy loss spectroscopy studies show, however, that the carbon in C_2N is sp^2 -hybridized rather than sp^3 -bonded carbon as in DLC. This carbon bonding in C_2N film leads to a high thermal stability that makes C_2N distinct from DLC and nitrogen doped DLCs, and thus an attractive candidate for applications. © 1996 American Institute of Physics. [S0003-6951(96)01019-4]

Carbon nitride materials have been the focus of considerable attention¹ since it was suggested that a solid analogous to beta silicon nitride, β - C_3N_4 , would have a hardness comparable to diamond.² While the synthesis of pure β - C_3N_4 remains an open challenge,³⁻⁸ it is also expected that carbon nitride phases distinct from β - C_3N_4 could exhibit attractive properties due to the short, covalent bonding between carbon and nitrogen. Unfortunately, past experimental studies have not identified unique carbon nitride stoichiometries and phases required for assessing the intrinsic physical properties of these materials. Recently, we have found that the stoichiometry C_2N represents a stable carbon nitride phase,⁹ and herein, describe the intrinsic physical properties and bonding in thin films of this material. C_2N exhibits high electrical resistivity and thermal conductivity similar to that of diamondlike carbon (DLC) films. Significantly, these diamondlike transport properties in C_2N come in a material consisting of sp^2 -bonded carbon versus the sp^3 -carbon of DLC. The diamondlike properties and nondiamondlike bonding make C_2N an attractive candidate for applications such as high-performance microelectronics.

Carbon nitride thin films containing up to ~50% nitrogen have been prepared by reacting laser ablated carbon with atomic nitrogen at a substrate surface.⁶ These as-deposited carbon nitride films, like those prepared by ion beam deposition and sputtering,^{4,5} are not pure phases and exhibit, for example, increasing amounts of $-C\equiv N$ impurity with increasing nitrogen composition above ~30%.^{6,9} Significantly, we have shown that a single carbon nitride product with C_2N stoichiometry is produced when the impurity is thermally eliminated from films containing initially $\geq 40\%$ nitrogen.⁹

The resistivity of C_2N is distinct from that observed for as-deposited carbon nitride films of similar composition [Fig. 1(a)]. Resistivity measurements made on as-deposited samples show an increase and then saturation at values between 10^3 and $10^4 \Omega \text{ cm}$ at 200 K as the initial nitrogen concentration increases above 40% [inset, Fig. 1(a)]. Typical temperature dependent resistivity data recorded on a film with 45% nitrogen, which were grown at 180 °C using a 532 nm Nd-YAG laser (0.75 J/cm² fluence) to ablate a pure

graphite target in the presence of atomic nitrogen, is shown in Fig. 1(a). The nitrogen content of this and other samples used in this study were determined by Rutherford backscattering spectroscopy. The resistivity of the C_2N sample obtained by annealing this film at 550 °C for 4 h in a vacuum

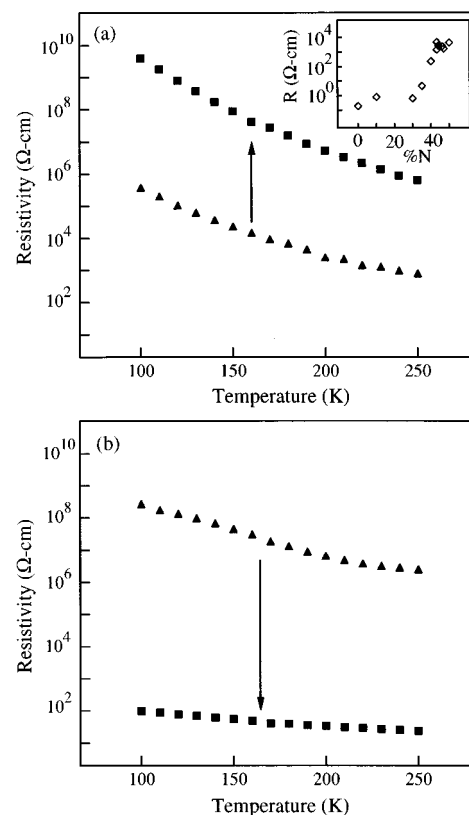


FIG. 1. Typical temperature dependent resistivity measurements made on (a) carbon nitride and (b) carbon samples before annealing (triangles) and after annealing (squares). (a) The carbon nitride sample contained 45% nitrogen before and 34% nitrogen after annealing. The composition was determined by Rutherford backscattering spectroscopy. The inset shows resistivity data recorded on as-deposited carbon nitride films as a function of the average nitrogen composition. The temperature dependent resistivity was determined for each of the carbon nitride samples, but only the value at 200 K is plotted. All data were obtained from four probe measurements (Keithley 220 current source and 6517 electrometer) on $\geq 1 \mu\text{m}$ thick samples that had been grown on quartz substrates. The carbon sample with initially 70% sp^3 bonding was grown at 240 K by laser deposition (532 nm, 23 J/cm² fluence) in a vacuum of 2.0×10^{-7} Torr.

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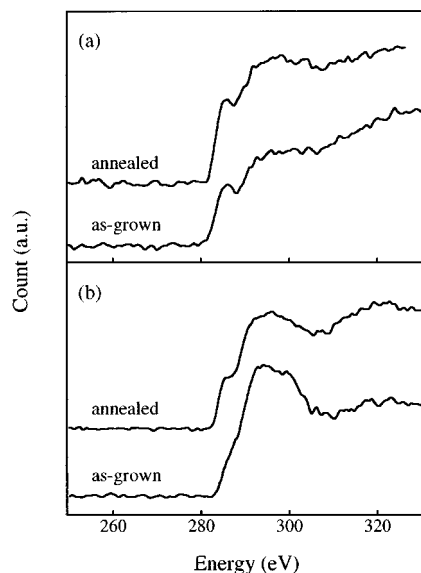


FIG. 2. (a) EELS data recorded on a carbon nitride sample containing 40% nitrogen before and 35% nitrogen after annealing. (b) Spectra recorded on a laser-deposited carbon film containing 70% sp^3 bonding before annealing and 30% sp^3 bonding after annealing. The spectra were recorded using a Philips EM 420 transmission electron microscope operating with a 120 keV beam energy and a Gatan 607 EELS detector.

4×10^{-8} Torr is 10^3 times larger than the as-grown film [Fig. 1(a)]. Furthermore, the resistivities of five independent C_2N products obtained from different starting materials are all similar, thus supporting our previous proposal⁹ that C_2N represents a relatively stable and well-defined phase. The large increase in resistivity observed after annealing is consistent with the elimination of the $C\equiv N$ impurity present in as-deposited carbon nitride samples, because this impurity is expected to create electronic states near the Fermi level that facilitate conduction. Indeed, analysis of the temperature dependent resistivity data using a variable-range hopping model supports this picture.¹⁰

It is interesting to compare the high resistivity C_2N material to DLC thin films since DLC is a likely competitor to carbon nitride in applications. DLC is an amorphous carbon material that contains a large fraction of sp^3 hybridized carbon.¹¹ In general, the properties of pure carbon samples are determined by the ratio of sp^3 : sp^2 -hybridized carbon: materials with large sp^3 fractions (e.g., DLC) will exhibit a high electrical resistivity like diamond, while materials with large sp^2 fractions will exhibit a low resistivity like graphite.¹¹ Significantly, the resistivity of a DLC film containing 70% sp^3 hybridized carbon [Fig. 1(b)], which is typical of DLCs reported previously,¹² is similar in magnitude to that observed for our C_2N samples. It is thus apparent that C_2N has diamondlike electrical properties.

The structural origins of the similar electrical properties of C_2N and DLC are, however, quite distinct. Electron energy loss spectroscopy (EELS) measurements of the carbon in C_2N samples exhibit a $1s-\pi^*$ transition at 285.5 eV characteristic of sp^2 hybridized carbon [Fig. 2(a)].¹³ Quantitative analysis of the EELS data¹⁴ shows that the as-grown carbon nitride sample contains $\sim 90\%$ sp^2 -hybridized carbon, and that after annealing the carbon in C_2N is all (98%) sp^2 -

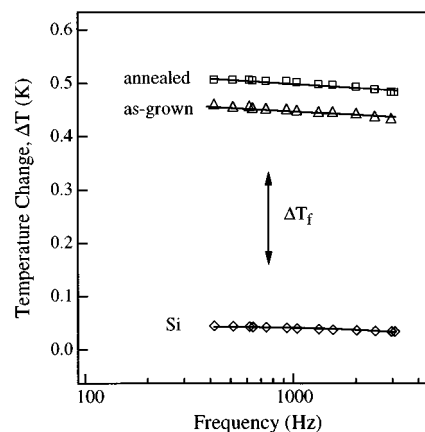


FIG. 3. Temperature change of gold lines deposited on a clean Si substrate (diamonds) and carbon nitride samples (triangles) as a function of the frequency of the ac current passed through the lines. The carbon nitride sample contained 43% nitrogen before (triangles) and 35% nitrogen after (squares) annealing. Measurements were made using 1500 Å thick gold lines with $b = 25 \mu m$ and $l = 2 mm$.

hybridized. Hence, the high electrical resistivity in C_2N can be associated with local trigonal bonding to carbon. EELS measurements made on DLC [Fig. 2(b)] show a high (70%) fraction of sp^3 -hybridized carbon; tetrahedral bonding of carbon is essential for insulating behavior in DLC. Indeed, when the fraction of sp^3 carbon is reduced by nitrogen implantation¹⁵ or annealing,¹⁶ DLC becomes much more conducting and graphite-like. C_2N is thus quite unique among reported carbon based thin films in that it exhibits diamondlike resistivity with graphite-like carbon hybridization.

The sp^2 -carbon hybridization in C_2N has important implications regarding its thermal stability compared to DLCs. One of important limitations of DLCs is their instability towards graphitization due to the high stress associated with sp^3 bonding within these amorphous materials. Thermal annealing of a DLC sample containing 70% sp^3 carbon at 550 °C for 2 h produces a carbon film containing only 30% sp^3 carbon [Fig. 2(b)]. The resistivity of the annealed sample is also 10^4 times smaller than the initial DLC value due to the growth of sp^2 -hybridized, graphite-like domains [Fig. 1(b)]. In contrast, C_2N is produced by this same annealing procedure and has a resistivity similar to as-deposited DLC. The C_2N is also essentially unchanged after annealing at 720 °C for 3 h in vacuum, and furthermore, exhibits limited stability even at temperatures as high as 800 °C. This high thermal stability of C_2N also contrasts the C–N polymer paracyanogen which decomposes completely between 675 and 695 °C.¹⁷ We believe that the high thermal stability of C_2N can be attributed to the relatively low stress sp^2 -hybridized carbon in this covalent solid, and expect that such stability could be of importance in both processing of multilayer structures and applications.

Diamondlike properties in addition to high electrical resistivity are required for applications. For example, thermal management in multichip modules and reduced dimension devices requires insulating materials with high thermal conductivity. DLCs, which exhibit both large electrical resistivity and thermal conductivity, have been proposed for such

applications, although deleterious sp^3 - sp^2 graphitization and substrate delamination has inhibited their use.¹⁸ The thermal stability and high resistivity of C_2N suggest that it might be an attractive alternative for these applications if it exhibits a reasonably high thermal conductivity. To address this point we have determined the thermal conductivity of our carbon nitride samples using an ac- 3ω electrical technique.¹⁹ In this method, the temperature change of a linear metal heater deposited on the carbon nitride sample, which can be related to thermal conduction through the film, is measured as a function of the ac current passing through the heater. Measurements made on carbon nitride and clean silicon substrates show that there is the expected¹⁹ frequency-independent temperature shift for the carbon nitride sample relative to the single-crystal substrate. The frequency independent temperature shift ΔT_f , of the carbon nitride samples is related to the thermal conductivity (Λ) by: $\Delta T_f = (P/l \cdot \Lambda)(t/2b)$, where P is the power at frequency 2ω , l and b are the length and width of the gold metal line, and t is the thickness of the carbon nitride film. From the magnitude of this shift we calculate that the thermal conductivity of C_2N is ~ 1 W/m K, although values as high as 1.5 W/m K have been observed in our samples. Significantly, the thermal conductivity of these carbon nitride samples is comparable to DLC and other thermally conducting amorphous materials.^{19,20}

In summary, we have shown that the carbon nitride compound C_2N exhibits diamondlike electrical resistivity and thermal conductivity. We believe it is significant that these diamondlike properties can be associated with a compound containing nondiamondlike sp^2 -hybridized carbon since these results highlight that C_2N is a unique material distinct from nitrogen-doped DLC and other nitrogen containing carbon materials studied previously. The high thermal stability of C_2N , which likely arises from its unstressed sp^2 carbon hybridization, the high electrical resistivity and thermal conductivity, and the fact that C_2N can be prepared by low-temperature deposition should make this material an attractive alternative to diamondlike carbons for demanding applications.

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