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UV Raman studies on carbon nitride structures

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Abstract Visible (514 nm) and deep UV (257 nm) Raman spectra of monoclinic tetracyanoethylene (tcne) are recorded at ambient conditions and also after laser heating at ambient pressure and at 40 GPa. Tetracyanoethylene ($C_2(CN)_4$) is a convenient precursor to synthesize hard C_3N_4 materials. At low incident laser powers the UV Raman spectra of virgin tcne resemble visible Raman spectra, and at higher powers there appear new, broad modes that increase in intensity as a function of laser power. When tcne is laser-heated at ambient pressure, there are two broad UV Raman peaks about 1,405 cm^{-1} and 1,604 cm^{-1} whereas visible laser Raman excitation results in too high a fluorescent background to show up any Raman modes. Raman spectrum of tcne laser heated at 40 GPa show broad peaks indicative of multiphase formation. The spectrum has additional modes at lower frequencies, and comparison with calculated Raman frequencies points to possible formation of α-C_3N_4.

Introduction

First principles calculations by Liu and Cohen [1] predicted that when synthesized, the bulk modulus (B) of β-C_3N_4 materials (of structure derived from the hexagonal β-Si_3N_4) would be comparable (at 427 GPa) to that of diamond (442 GPa). Later calculations by Teter and Hemley [2] indicated that other hard structures of C_3N_4 are possible, and that a high pressure cubic phase would possess even higher bulk modulus (496 GPa). These expectations have led many experimental groups to attempt synthesizing such tetrahedrally bonded materials using a variety of techniques such as sputtering [3–5], chemical precursor technique [6, 7], ion-beam deposition [8], pulsed laser-induced liquid-solid interfacial reaction [9], dc sputtering [4], chemical vapour deposition [10, 11], shockwave compression of carbon–nitride precursor [12], ion-beam assisted pulsed laser deposition [13, 14], nitrogen ion implantation into diamond surface [15], and high pressure [16–21]. Considerable theoretical work has also been done on various aspects of these solids [22–25]. Most of the deposition attempts have resulted in amorphous films with a mixture of sp, sp^2 and sp^3 bonding. Systematic electron energy loss spectroscopic (EELS) studies have indicated that it may be difficult to obtain sp^3 bonded C_3N_4 using physical deposition methods, since as the nitrogen concentration in the film increases to above 11%, there is a preference to form sp^2 bonded carbon [26]. Several claims of growth of crystalline β-C_3N_4 films on closer scrutiny turned out to be of dubious validity (for an extensive review, see [27]). High pressure-high temperature synthesis starting from suitable carbon nitride precursors is seen as a promising way of bulk synthesis of hard C_3N_4 structures. It is noteworthy that recently superhard cubic BC_2N—with hardness exceeding that of cBN that held the record for being the second hardest material for 45 years—has been synthezized from graphite-like BC_2N at pressures

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exeeding 18 GPa and temperatures higher than 2,200 K [28].

There are some recent reports of successful deposition of crystalline grains of microscopic dimensions [4, 10]. Characterization was done by techniques such as X-ray and electron diffraction, scanning and transmission electron microscopy, infrared and Raman spectroscopy, and X-ray photoelectron spectroscopy. β-C_3N_4 structure has also been formed by low-energy nitrogen ion-implantation into a diamond surface [15]. Hardness of these films is yet to be measured, and it is clear that bulk synthesis is desirable for hardness measurement and many other applications, though hard thin films would find important applications themselves.

One of the more promising attempts to produce crystalline C_3N_4 seem to be those of Y. Chen et al. [29], who synthesized thin crystalline films of α and β-C_3N_4 on nickel substrates by a hot filament CVD technique. They obtained well faceted hexagonal crystals of length up to several hundred micrometers and hundreds of nanometer cross section, with N:C ratio between 1.3 and 1.4. The measured lattice constants agree with the theoretically predicted values. Raman spectra of these crystals [30] exhibited several well-defined, sharp peaks at expected positions, in contrast to all other known reports claiming synthesis of crystalline C_3N_4 that exhibited only a few broad peaks. However, this claim of synthesis of α and β-C_3N_4 has been questioned by Matsumoto et al. [31] since the observed d values are 1.3–2.5% smaller than those estimated theoretically [2]. Also, some reflections with larger d values were absent in the XRD patterns and some of the intensities do not match with calculated ones. Matsumoto et al. [31] in fact scrutinized about 70 papers and concluded that there is no definite evidence for the synthesis of any of the crystalline forms of C_3N_4 at that time.

A more recent publication by Zhang et al. [32] reports synthesis of a mixture of α and β-C_3N_4 films on Si(100) substrate by a microwave plasma CVD technique that produced hexagonal crystalline rods of 1–2 μm length and ~0.4 μm width. All strong peaks expected of α and β-C_3N_4 were present. Infrared and Raman spectra of these films exhibited fairly sharp and strong peaks at expected positions [33].

An attempt to synthesize bulk carbon nitride crystals at high pressures and high temperatures has been reported [34]. The authors employed a belt-type high pressure apparatus, and subjected $C_3N_4H_4$ powder to 7 GPa and 1,400 °C for 10 min in contact with a flat surface of metal catalysts. While $C_3N_4H_4$ turned into graphite, the surface of the catalyst was coated with micron-sized CN crystals that could be identified by X-ray diffraction as consisting of α and β phases of C_3N_4.

So far none of the attempts have yielded bulk, hard C_3N_4 structures. There are even questions whether these hypothetical materials could ever be synthesized by any technique at all. Energetically, the most stable species is rhombohedral C_3N_4 that is structurally graphite-like and presumably soft. Also, increasing realization that Vickers hardness (V_H) of a material, particularly carbon–nitrogen materials, is proportional to its shear modulus rather than bulk modulus [35], has dampened the enthusiasm to some extent, since the predicted shear modulus of cubic C_3N_4 is lower (332 GPa) than that of diamond (535 GPa). At present, synthesis of a carbon-nitride material harder than diamond seems like a dream. Nevertheless, it is clear that the byproducts of research on hard C_3N_4 materials themselves are interesting and useful, and this line of research is worth pursuing. Brazhkin et al. [36], and McMillan [37] have recently reviewed the current status and methods to synthesize superhard materials, and high pressure methods have been recommended as promising techniques.

It is worth mentioning here that attempts to synthesize all-carbon hard materials from C_{60} by high pressure, high temperature techniques have yielded promising results, and synthesis of diamond at room temperature [38–40] and harder-than-diamond materials [41, 42] have been reported.

A major problem encountered in work on synthesis of tetrahedrally bonded materials such as diamond-like carbon (DLC, also known as tetrahedral amorphous carbon, t-aC) and carbon–nitrogen structures is that of identification of sp^3 and sp^2 bonding. Transmission electron energy loss spectroscopy (EELS) is an important and widely used tool for this purpose, but it seems to be not really effective since the energies of these two bonds are too close to be resolved satisfactorily. UV Raman spectroscopy on the other hand could distinguish between the two bonding types since the Raman modes of diamond (sp^3 bonded carbon) and graphite (sp^2) are separated by as much as 250 cm^{-1}, and unlike visible excitation, UV excitation gives evenly weighted spectral intensities of sp^2 and sp^3 vibrations. The problem of fluorescence from sp^2 species is overcome since there is no fluorescence in the UV region where the spectra are collected, but only visible fluorescence under UV excitation. Only relatively recently has the potential of UV Raman spectroscopy come to be appreciated [43–45].

Tetracyanoethylene (tcne) is a convenient starting material in endeavors to produce C_3N_4 materials. It contains several unsaturated bonds (four $C \equiv N$ and one C–N) that could open under pressure, so it could serve as a precursor to carbon–nitrogen polymers that would not be restricted to linear geometry but could lead to two or three dimensional networks. There have been some attempts to synthesize the hypothetical *β* and other C_3N_4 structures by high pressure-high temperature techniques [16, 17] starting from tcne. Here we report UV Raman studies on tcne (i) at ambient pressure, (ii) laser heated at ambient pressure and (iii) laser heated at high pressure, in order to determine the effects of pressure and temperature on tcne. We find that even at ambient pressure this material polymerizes at low levels of UV radiation used to excite the Raman spectra. High temperature alone does not seem to have a major effect on the Raman spectra, but the combined effect of high pressure and high temperature seems to transform tcne into a mixture of C_3N_4 structures.

Experimental

TCNE obtained from Alfa Aeser was vacuum sublimated and monoclinic crystals grown by evaporating a solution of ethyl acetate at 300 K. X-ray diffraction pattern was recorded to confirm the structure. A yttrium-lithium-fluoride (YLF) laser ($\lambda = 1.054$ micron) was used to heat the sample crystallites which had been placed in a 165 micron hole in a stainless steel gasketed Mao-Bell type diamond anvil cell, sandwiched between alumina powder. The crystallites that were white in the beginning became more transparent on laser heating for a few seconds. Visible (514 nm) Raman spectra were recorded in situ by means of Dilor micro-Raman spectrometer equipped with a liquid nitrogen cooled CCD detector (Princeton Instruments). UV Raman spectra were recorded on the retrieved sample at ambient pressure with separate micro Raman spectrometer in a single monochromator configuration. A 257 nm Coherent FRED intracavity frequency-doubled argon ion laser was used for excitation. More details on this set up could be found in [46].

Results and discussion

Figure 1 shows the UV Raman spectrum of tcne at a low incident power, and also the visible Raman spectrum for comparison.

The visible Raman spectrum corresponds closely to the literature data [47]. In the UV Raman spectrum, only the most intense peaks, at 1,568 cm^{-1} and 1530 cm^{-1}, are seen. This could be due to the difference in scattering cross section of the various phonons to the UV photon.

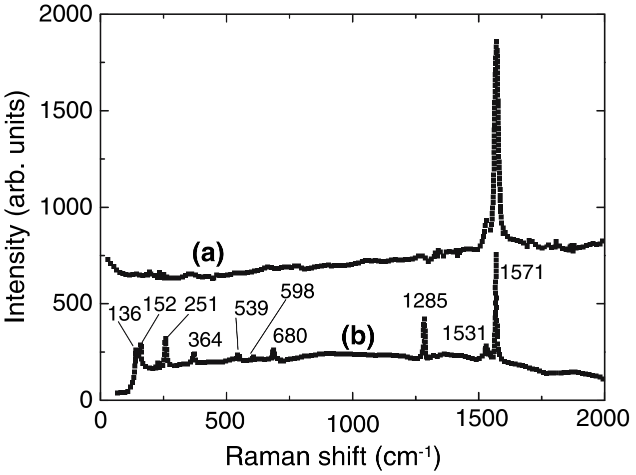

Fig. 1 Raman spectra of tetracyanoethylene (tcne: $C_2(CN)_4$) with (**a**) 257 nm UV laser excitation and (**b**) 514 nm visible laser excitation. In the UV Raman spectrum, only the most intense peaks are seen

When the incident power is increased, the intensity of the 1,568 cm^{-1} is reduced and a new, broad peak starts developing about 1,612 cm^{-1} (Fig. 2); broad peaks appear about 1,387 $cm^{-1}$and 1,442 cm^{-1} also. Visual inspection reveals that the sample, initially white in color, has become slightly brownish. When the incident power is increased, the 1,612 cm^{-1} peak increases in intensity, envelops and merges with the 1,568 cm^{-1} peak. The overall intensity between 1,000 cm^{-1} and 1,800 cm^{-1} increases, and modes of low intensity develop around 760 cm^{-1} and 1,000 cm^{-1}. It is clear that UV radiation links up the tcne molecules

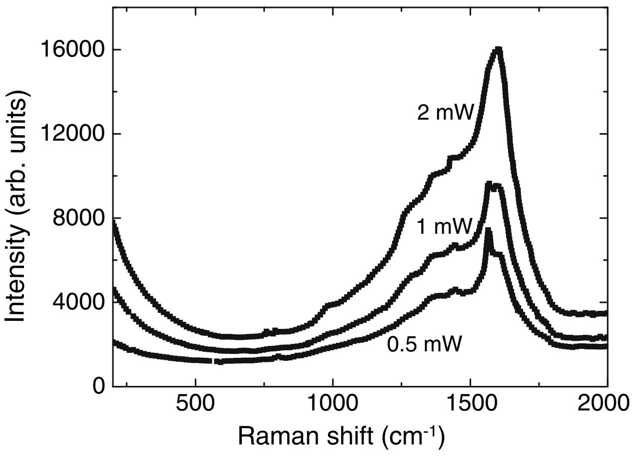

Fig. 2 UV Raman spectra of tcne at different incident laser powers. UV laser has a profound effect on tcne

in some manner to produce a polymeric structure responsible for broad vibrational modes. The sample was seen to be turning increasingly dark as the incident power is increased.

The UV Raman spectrum of the sample laser heated at ambient pressure in a diamond anvil cell showed two broad peaks, at 1,370 cm^{-1} and 1,576 cm^{-1} (Fig. 3). They could arise as a result of merging of 1,387, 1,442 cm^{-1} and 1,568, 1,612 cm^{-1}, respectively of Fig. 2. A peakfit analysis of a spectrum in Fig. 3 in fact revealed peaks about 1,343, 1,428, 1,557, 1,581 besides a broad peak about 1,276 cm^{-1}. The first four peaks are close to those of Fig. 2.

It is known from literature [48] that at pressures above 14 GPa, tcne transforms into an amorphous polymeric phase. When tcne is laser heated at 40 GPa (hereafter referred to as HP-HT sample) and the UV Raman spectrum recorded on the retrieved sample at ambient pressure, the 1,405 cm^{-1} peak has broadened, and new broad peaks have developed about 740 cm^{-1} and 1,000 cm^{-1}. This indicates that the sample has turned into a multiphase material, and vibrational assignment of broad bands is rather tricky. Using peak-fit software this spectrum could be automatically resolved into its component features as shown (Fig. 4).

Wada et al. [49] using group theoretical analyses calculated the number of possible Raman and infrared active modes of crystalline α-Si_3N_4 and β-Si_3N_4. For α-Si_3N_4, 40 optically active modes are expected, all of which are both infrared and Raman active, whereas for β-Si_3N_4 11 Raman active modes and 6 infrared active modes are expected. Experimentally, 30 Raman and 18 infrared modes were observed for α-Si_3N_4 whereas for the β phase the observations tally with group theoretical prediction [49].

Zhang and Gu [33] have calculated the Raman peaks expected of α-C_3N_4 by scaling up by a factor of 1.43 the Raman frequencies of α-Si_3N_4 [49]. The scaling factor 1.43 was obtained from a consideration of β-Si_3N_4 data by an anonymous reviewer to Wixom's manuscript [12] suggesting the use of Hooke's law to calculate C–N stretching frequencies from those of C–C frequencies, since force constants scale linearly with bulk modulus and bond length. The calculated the Raman peaks expected of α-C_3N_4 [33] in the frequency

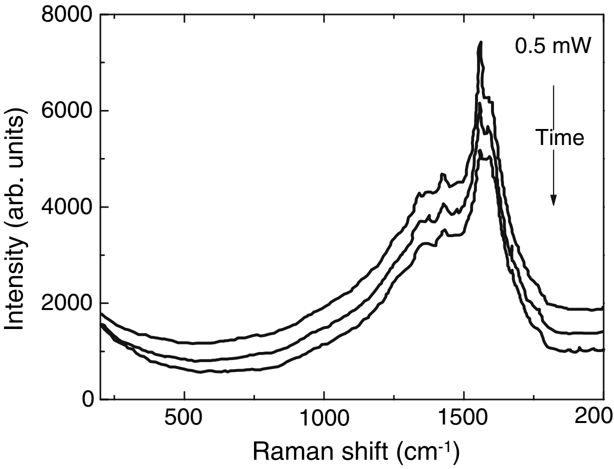

Fig. 3 UV Raman spectrum of the sample laser heated at ambient pressure in diamond anvil cell showed two broad peaks at 1,604 cm^{-1} and 1,405 cm^{-1}. They could arise as a result of merging of 1,568, 1,612 cm^{-1}, and 1,387, 1,442 cm^{-1}, respectively of Fig. 2

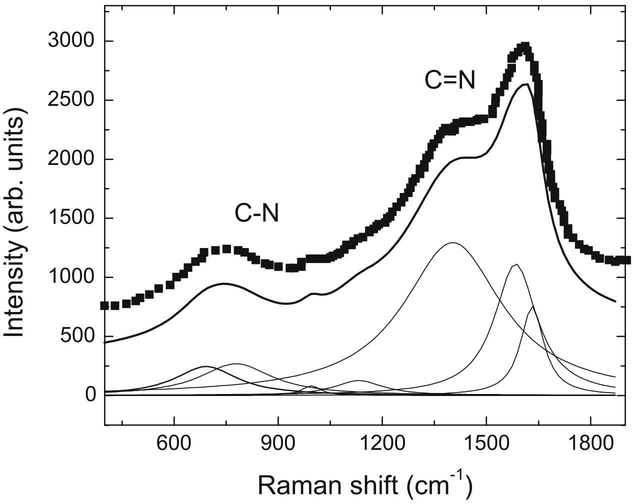

Fig. 4 UV Raman spectrum at ambient conditions, of tcne laser heated at 40 GPa. ■— Experimental spectrum. Lorentzian peaks at the bottom make up the continuous curve that fits the experimentally observed spectrum (displaced for clarity)

Table 1 Comparison of Raman modes calculated for a crystalline thin film of α-C3N4 [33] with the present results

Zhang et al [30] (Partial list) Raman shift (cm^{-1})	Present results of Raman shift (cm^{-1})
676	–
691	692
765	–
789	779
836	–
883	–
980	995
1,016	–
1,122	1,132
1,247	–
1,276	–
1,398	–
1,433	1,403
1,517	1,584
1,627	1,632
1,679	–

region of interest are tabulated (Table 1) along with those obtained from the present HP-HT sample spectrum. It is seen that there is good match between the seven peak frequencies obtained for the HP-HT sample and α-C_3N_4, leading to the conclusion that α-C_3N_4 phase should be present in the HP-HT sample.

Visible (514 nm excitation) Raman spectra of laser heated samples showed only high and nearly constant fluorescence in the entire range.

Ferrari et al. [50] have carried out detailed studies of infrared and Raman spectra of amorphous carbon nitrides, leading to the following criterion [51]: if the sample contains only sp^3-bonded species, the position of the 'G-peak' (that occurs between 1,480 cm^{-1} and 1,600 cm^{-1} for different types of carbon) does not change if the laser excitation energy is changed (e.g., from visible 514 nm to UV 257 nm). If it has sp^2-bonded species, this peak position changes. Since, as mentioned above, the visible Raman spectra could not be acquired due to high fluorescence, this could not be tested in the present studies.

Summary

We have reported an attempt to synthesize crystalline C_3N_4 by laser heating tetracyanoethylene ($C_2(CN)_4$) at 40 GPa. UV Raman spectra of this HP-HT sample indicated formation of multiphase material. The frequencies of the broad peaks are close to those expected for α-C_3N_4, indicating possible formation of this phase along with other phases. It appears that high-pressure—high-temperature route is a promising technique in attempts to synthesize bulk C_3N_4 phases. More studies are needed to optimize the pressure and temperature conditions.

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