The Embedded Ring Approach Applied to Annealed Graphitic Amorphous Carbon

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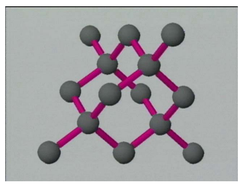
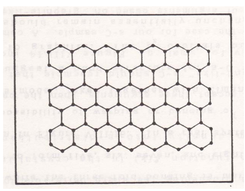
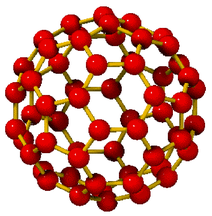
FORMS OF CARBON



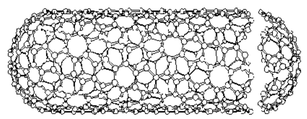
DIAMOND is a 3-D crystal, where the carbon atoms are bonded to 4 neighbors with four-fold sp^3 bonding. This crystalline sp^3 bonding is what gives diamond its extremely hard properties.



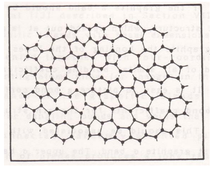
GRAPHITE has 3 carbon atoms bonded to one another with three-fold sp^2 bonding, leading to a planar hexagonal arrangement . The planes are weakly bonded to each other, thus they can slide past each other, lending to the lubricant nature of graphite.



BUCKYBALLS consist of 60 carbon atoms in 5-membered and 6-membered rings curled up on themselves to form a ball. A property of buckyballs which has been recently discovered is that they can form high temperature superconductors.



NANOTUBES are a sheet of graphite rolled up, often with buckyball-like caps on the ends. The technological advantages of nanotubes, from semiconductor properties and quantum wires to material strength, are only beginning to be exploited.



GRAPHITIC AMORPHOUS CARBON has no long range order. It is believed to have a mostly planar structure, like graphite, but contains 5- and 7-membered rings in addition to hexagonal rings. This research explores the microscale structure of graphitic amorphous carbon

WHY STUDY AMORPHOUS CARBON?

Graphitic amorphous carbon is not as technologically important as other forms of carbon. However, in the process of synthetically making diamonds, graphite, buckyballs, and nanotubes, graphitic amorphous carbon (g-C) is also produced. A better understanding of the structure and bonding process of g-C could lead to more efficient synthesis of the above listed technologically valuable materials and pave the way for constructing yet unimagined carbon structures.

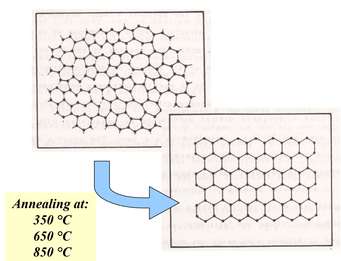
QUESTION: HOW DOES THE MICROSCALE STRUCTURE OF GRAPHITIC AMORPHOUS CARBON CHANGE WITH ANNEALING TEMPERATURE?

ABSTRACT

Determination of the nanoscale structure and bonding of atoms in highly disordered materials is extremely difficult, but essential in understanding these ubiquitous materials. We perform complex calculations that allow the determination of the medium range order of constituent atoms in graphitic amorphous carbon (g-C) by modeling its Raman spectra, which correspond to the in-plane motion of atoms. Specifically, a dynamical model, the embedded ring approach (ERA), is applied to predict the evolution of vibrations and structure of annealed g-C. We find that the graphitic nature of g-C increases with annealing temperature as evidenced by a greater fraction of 6-membered rings and by sharper peaks in the Raman spectra.

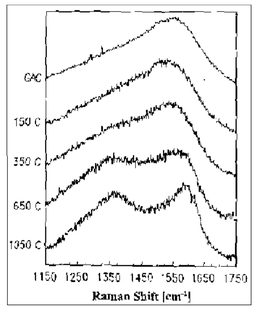
PROCEDURES

Step 1: Anneal the Graphitic Amorphous Carbon



It is known that annealing graphitic amorphous carbon (g-C) by heating it up to a high temperature for an extended amount of time allows atoms and bonds in g-C to rearrange and reach the lowest energy equilibrium structure, which is graphite. However, at intermediate temperatures for a less amount of time, the effects of annealing on the evolution of the microscale structure of g-C are not well understood.

Step 2: Collect Data of the Raman Spectra



The qualitative effects of annealing on the structure of graphitic amorphous carbon can readily be seen in the development of two peaks in the Raman spectra. Raman spectroscopy is a probe of the in-plane motion of the carbon atoms.

Step 3: Computationally Analyze the Spectra

The ring statistics of graphitic amorphous carbon can be determined by fitting the overall Raman spectra with the individual spectra contributed by each size of ring. Mathematically this is:

$$\text{Fit} = \sum_{j=5}^{7} G\left(\omega, \sigma_A, I_{A_j}, P_A\right) + \sum_{j=5}^{7} G\left(\omega, \sigma_E, I_{E_j}, P_E\right)$$

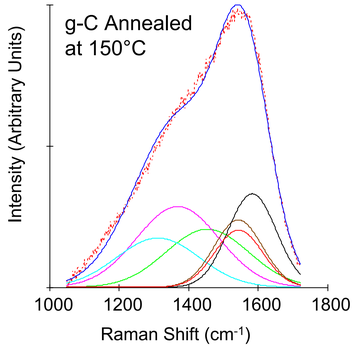
where the function G is a Gaussian line shape defined on the domain of ω with a standard deviation of σ and an integrated area of $I_{A,E}$ centered around the mode frequencies $P_{A,E}$ as given by the Embedded Ring Approach.

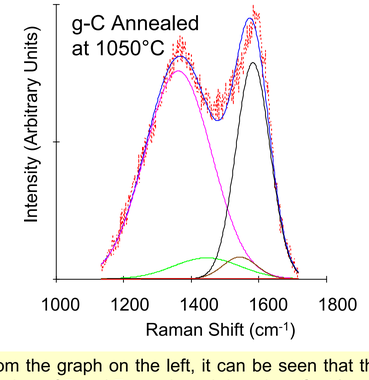
The ring statistics for a particular ring size are then determined from the fit by

$$\text{Percent} = \frac{I_i}{I_5 + I_6 + I_7} \cdot 100\,\%$$

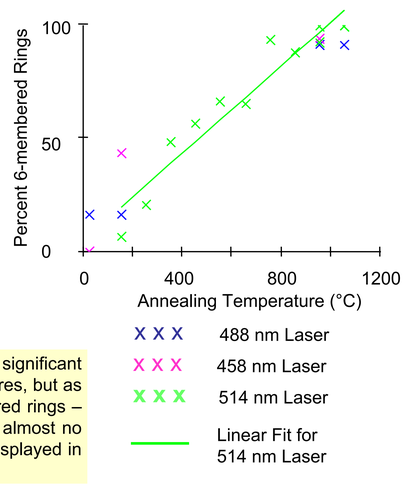
where the i^{th} intensity, I_i, is the sum of the i^{th} A mode intensity, I_{Ai}, and the i^{th} E mode intensity, I_{Ei}, for i=5,6,7.

RESULTS AND CONCLUSIONS





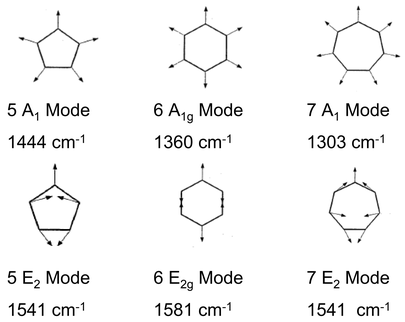
From the graph on the left, it can be seen that there are a significant number of 5 and 7-membered rings in g-C at low temperatures, but as seen above, these rings have been converted to 6-membered rings – namely nanocrystalline graphite. The continual trend from almost no 6-membered rings to predominantly 6-membered rings is displayed in the graph on the right.



THE EMBEDDED RING APPROACH

Although there is no long range order in amorphous materials, groups of 8 or less atoms can be arranged in rings. These rings do not exist independently from the rest of the material, but are embedded in it. Each ring size has vibrational modes and frequencies associated with it.

RAMAN-ACTIVE MODES



5 A_1 Mode	6 A_{1g} Mode	7 A_1 Mode
1444 cm^{-1}	1360 cm^{-1}	1303 cm^{-1}
5 E_2 Mode	6 E_{2g} Mode	7 E_2 Mode
1541 cm^{-1}	1581 cm^{-1}	1541 cm^{-1}

FUTURE OF THE EMBEDDED RING APPROACH

In addition to the in-plane modes and frequencies shown above, the Embedded Ring Approach (ERA) will be used to calculate the out-of-plane modes and frequencies. Infrared spectroscopy is used to detect such out-of-plane motions. The same analysis will be performed on the spectra in order to look for a correlation of ring statistics between the Raman and the Infrared spectra. Close correlation of ring statistics between the two different spectra will verify that the ERA is a valid vibrational model of amorphous carbon and any other planar amorphous material. The furthest extension of the ERA would be to 3-d amorphous materials.

REFERENCES

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