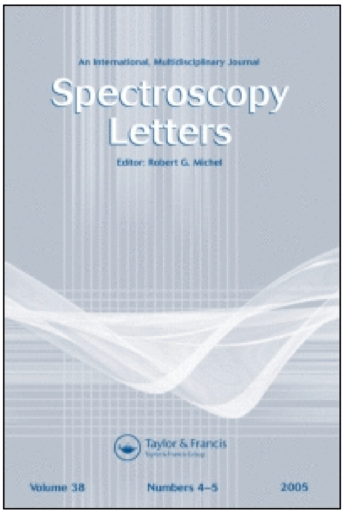
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# Pressure-Induced Modification of Hydrogenated Amorphous Carbon

J. C. Corcoran[a]; S. A. Lee[a]
[a] Department of Physics and Astronomy, University of Toledo, Toledo, OH, USA

**To cite this Article** Corcoran, J. C. and Lee, S. A.(1993) 'Pressure-Induced Modification of Hydrogenated Amorphous Carbon', Spectroscopy Letters, 26: 4, 565 — 574

**To link to this Article: DOI:** 10.1080/00387019308011554

**URL:** http://dx.doi.org/10.1080/00387019308011554

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 26(4), 565-574 (1993)

# PRESSURE-INDUCED MODIFICATION OF HYDROGENATED AMORPHOUS CARBON

Key Words: Photoluminescence spectroscopy; High pressure effects; Hydrogenated amorphous carbon

J.C. Corcoran and S.A. Lee

Department of Physics and Astronomy
University of Toledo
Toledo, OH 43606 USA

## ABSTRACT

Photoluminescence spectroscopy has been used to study the effects of high pressure on hydrogenated amorphous carbon. Irreversible changes are observed in samples pressurized above 9.0 GPa.

## INTRODUCTION

Interest has grown recently in hydrogenated amorphous carbon (HAC) because of its high hardness and significant optical gap (0.5 - 2.0 eV) and the relative ease with which it can be produced. These important properties of HAC are due to its microstructure, i.e., the type of bonding of the carbon atoms and the role of the hydrogen. The carbon atoms have both $sp^3$ and $sp^2$ types of bonding in these networks as shown by a variety of experimental techniques: electron-energy-loss spectroscopy (EELS),[1] electron spin resonance (ESR) spectroscopy,[2] near edge absorption spectroscopy,[3,4] and infrared spectroscopy.[5] The correlation between the optical gap and the Raman spectra indicates that the optical properties are determined by compact π-bonded clusters composed of approximately 10-100 aromatic rings.[6] The optical gap of such clusters varies as $6.0/N^{1/2}$ (eV), where N is the number of rings.[7]

Tamor and Wu have developed the "defected graphite" (DG) model to explain the large body of experimental data available for HAC.[8] In graphite, all of the carbon atoms have $sp^2$ bonding and form sheets. The π electrons in graphite are completely delocalized and cause graphite to be a semimetal. The fact that an appreciable optical gap is observed in HAC shows that a significant fraction of the carbon atoms have $sp^3$ hybridization. In the DG model, defects are either a carbon atom vacancy or a carbon atom with $sp^3$ bonding. Hydrogen is incorporated in the network by passivating "dangling" bonds at such defect sites.

High pressure techniques have shown that amorphous insulators such as $SiO_2$ and $GeO_2$ can be irreversibly modified by the application of pressure. Grimsditch[9] found that the product of the refractive index and the speed of sound changed irreversibly in $SiO_2$ samples which were pressurized to 16 GPa (1 GPa = 9869 atm), indicating that a new form of amorphous $SiO_2$ had been formed. Hemley *et al.*[10] used *in situ* Raman scattering to study changes in the $SiO_2$ network during compression. They found that reversible changes in the Si-O-Si bond angles were induced up to 8 GPa. Higher pressures caused irreversible changes in the bond angles along with a shift in the average number of atoms in rings within the network. Itie *et al.*[11] used x-ray absorption spectra on amorphous $GeO_2$ to show that the coordination of Ge changes from fourfold to sixfold at pressures between 7 and 9 GPa. These results suggest that high pressure can be used to modify amorphous networks and the average coordination number for insulators.

No report has yet appeared in the literature to report such irreversible behavior in an amorphous semiconductor. In this Letter, we report our room temperature study of the photoluminescence (PL) properties of HAC (an amorphous semiconductor) up to 10 GPa of pressure. The fact that HAC is amorphous causes its PL to be very broad.[12,13] Changes observed in the PL indicate a modification to the electronic properties of our samples.

## EXPERIMENTAL

HAC was produced in the form of thin films by use of an rf glow discharge tube with methane used as the deposition medium. Small pieces of these films (about 50 μm in diameter) were loaded into a miniature Merrill-Bassett diamond anvil cell.[14] The sample was contained in a 250 μm diameter hole in an Inconel X-750 gasket. A 4:1 mixture of methanol and ethanol was used as the pressure-transmitting medium.[15] Such mixtures have been shown to be hydrostatic at room temperature up to 10 GPa.[15] Small pieces of ruby were also placed in the sample chamber. The frequency of the $R_1$ and $R_2$ fluorescence of ruby is pressure-dependent and has been calibrated.[16] Thus, *in situ* measurements of the pressure were made. No significant broadening of the $R_1$ and $R_2$ peaks was observed in any experiments, indicating that there were no significant pressure gradients.

The photoluminescence spectra were excited by using about 200 Mw of 4880 Å light from an argon-ion laser. Backscattered light was focussed into a double monochromator and detected with a photomultiplier tube. Standard photon counting electronics were controlled by an IBM PC-XT to acquire the signal.

## RESULTS AND DISCUSSION

A typical photoluminescence spectrum from HAC (at 2.57 GPa) is shown in Fig. 1. All of the PL spectra were of the same general shape. As the pressure on the HAC is increased, the position of the peak moves to

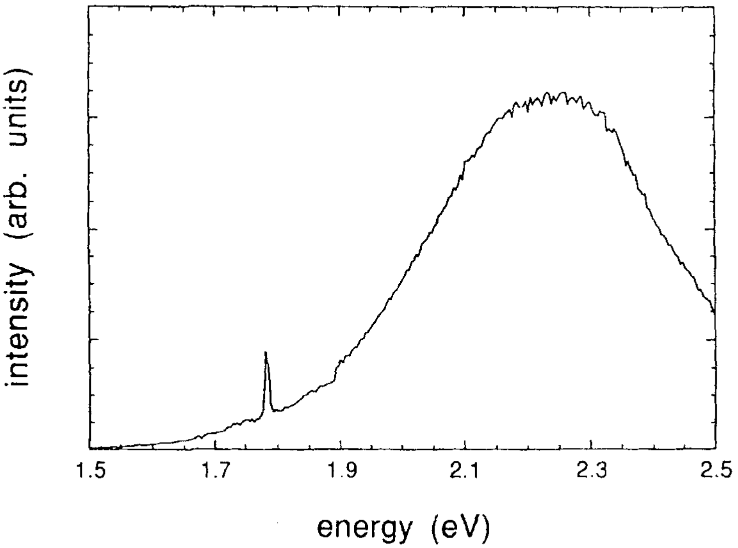


Fig. 1 The photoluminescence signal from HAC at 2.57 GPa and room temperature. The sharp feature near 1.78 eV is due to the ruby fluorescence.

higher energies. An examination of Fig. 1 shows that it is difficult to locate the maximum of the PL spectra accurately due to its large width. Two different techniques were used: 1.) a third-order polynomial was fitted to the top of the peak and the maximum of this polynomial was determined by setting its derivative equal to zero; and 2.) the position of the peaks were determined by visual inspection. The results of the two procedures were virtually indistinguishable. In order to eliminate any possible human biases, only the results of the third-order polynomial fits are reported here.

Figs. 2 and 3 show the peak position of the PL as a function of both increasing and decreasing pressure for two different samples. Both figures show that the peak position shifts to higher energy as the pressure is increased. This indicates that the band gap is widening as the pressure is increased. This behavior cannot continue to arbitrarily high pressures as all materials will become metallic when compressed sufficiently. However, this initial increase of the band gap with pressure has been observed in many semiconductors. For instance, the band gap in GaAs initially increases at a rate of +107.3 meV/GPa.[17]

The maximum pressure attained in Fig. 2 was 9.0 GPa while the maximum pressure attained in Fig. 3 was 9.5 GPa. Notice that significant hysteresis is observed as the pressure is lowered in both figures. However, upon return to atmospheric pressure, the peak position of Fig. 2 returns to the (essentially) the same value as the PL peak in the unpressurized sample. Fig. 3 shows that the peak position does **not** return to its unpressurized value.

The irreversible shift of the peak position for a sample pressurized to 9.5 GPa is evidence that the HAC sample has been changed in an irreversible manner by the application of pressure. Samples raised to a lower maximum pressure ($\leq$ 9.0 GPa) did not show these irreversible changes. Consequently, the critical pressure for irreversible changes is between 9.0 and 9.5 GPa.

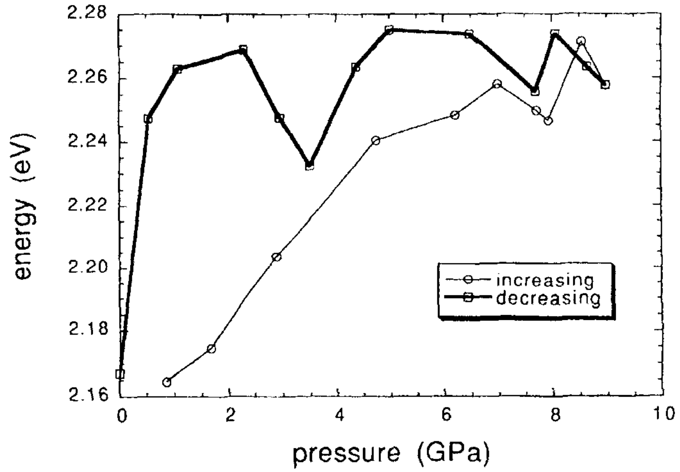


Fig. 2 Plot of the maximum intensity of the photoluminescence signal from HAC as a function of pressure. The maximum pressure for this sample was 9.0 GPa. The circles (o) are for increasing pressure and the squares (□) are for decreasing pressure. The solid lines are merely guides for the eye.

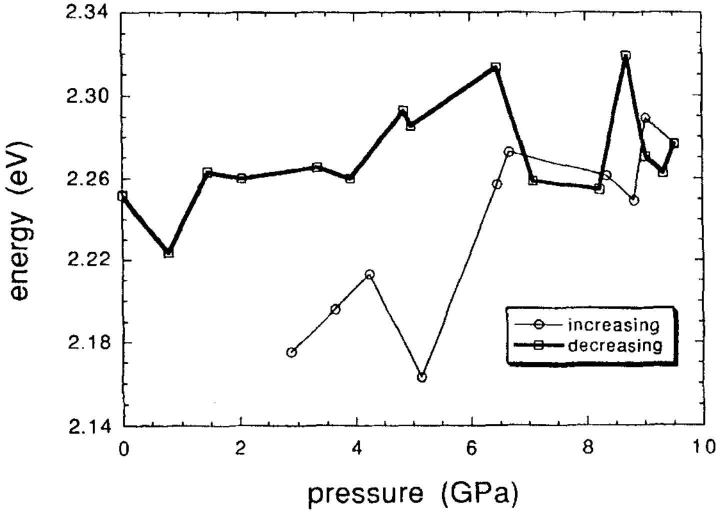


Fig. 3 Plot of the maximum intensity of the photoluminescence signal from HAC as a function of pressure. The maximum pressure for this sample was 9.5 GPa. The circles (o) are for increasing pressure and the squares (□) are for decreasing pressure. The solid lines are merely guides for the eye.

At the present time not enough experimental evidence is available to determine the microscopic nature of this irreversible change. Two possible explanations are 1.) an irreversible densification of the sample; or 2.) an irreversible change in the bonding of the network (i.e., the relative amounts of $sp^2$ and $sp^3$ bonding). It would seem reasonable that the network might be irreversibly densified at a lower pressure than necessary to change the bonding. However, the maximum pressure necessary to change the PL spectrum irreversibly is within the pressure range for changes in the bonding. As discussed earlier, bonding changes occur in amorphous $SiO_2$ beginning at about 8 GPa and in amorphous $GeO_2$ between 7 and 9 GPa.

## SUMMARY

The application of high pressure to samples of hydrogenated amorphous carbon causes the photoluminescence to shift to higher energies, indicating that the energy gap between the corresponding electronic states is widening. Irreversible changes have been observed in the PL spectra of samples raised to pressures on the order of 9.5 GPa while samples raised to 9.0 GPa did not display any irreversible changes. This indicates that the "critical" pressure for such irreversible changes is between 9.0 and 9.5 GPa. This is the first report of such irreversible pressure-induced changes in an amorphous semiconductor.

## REFERENCES

1. Weissmantel, C., Bewilogua, K., Breuer, A.K., Dietrich, D., Eberbach, U., Erler, H.-J., Rau, B., Reisse, G. Preparation and Properties of Hard i-C and i-BN Coatings. *Thin Solid Films* 1982; **96**: 31.

2. Gambino, R.J., Thomson, J.A. Spin Resonance Spectroscopy of Amorphous Carbon Films. *Solid State Commun.* 1980; **34**: 15.

3. Wesner, D., Krummacher, S., Carr, R., Sham., T.K., Strongin, M., Eberhardt, W., Weng, S.L., Williams, G., Howells, M., Kampas, F., Heald, S., Smith, F.W. Synchrotron-Radiation Studies of the Transition of Hydrogenated Amorphous Carbon to Graphitic Carbon. *Phys. Rev. B* 1983; **28**: 2152.

4. Fink, J., Müller-Heinzerling, Th., Pflüher, J., Bubenzer, A., Koidl, P., Crecelius, G. Structure and Bonding of Hydrocarbon Plasma Generated Carbon Films: An Electron Energy Loss Study. *Solid State Commun.* 1983; **47**: 687.

5. Dischler, B., Bubenzer, A., Koidl, P. Bonding in Hydrogenated Hard Carbon Studied by Optical Spectroscopy. *Solid State Commun.* 1983; **48**: 105.

6. Tamor, M.A., Haire, J.A., Wu, C.H., Hass, K.C. Correlation of the Optical Gaps and Raman Spectra of Hydrogenated Amorphous Carbon Films. *Appl. Phys. Lett.* 1989; **54**: 123.

7. Robertson, J., O'Reilly, E.P. Electronic and Atomic Structure of Amorphous Carbon. *Phys. Rev. B* 1987; **35**: 2946.

8. Tamor, M.A., Wu, C.H. Graphitic Network Models of "Diamondlike" Carbon. *J. Appl. Phys.* 1990; **67**: 1007.

9. Grimsditch, M. Polymorphism in Amorphous $SiO_2$. *Phys. Rev. Lett.* 1984; **52**: 2379.

10. Hemley, R.J., Mao, H.K., Bell, P.M., Mysen, B.O. Raman Spectroscopy of $SiO_2$ Glass at High Pressure. *Phys. Rev. Lett.* 1986; **57**: 747.

11. Itie, J.P., Polian, A., Calas, G., Petiau, J., Fontaine, A., Tolentino. H. Pressure-Induced Coordination Changes in Crystalline and Amorphous $GeO_2$. *Phys. Rev. Lett.* 1989; **63**: 398.

12. Robertson, J. Amorphous Carbon. *Adv. Phys.* 1986; **35**: 317.

13. Street, R.A. Luminescence in Amorphous Semiconductors. *Adv. Phys.* 1976; **25**: 397.

14. Jayaraman, A. Diamond Anvil Cell and High-Pressure Physical Investigations. *Rev. Mod. Phys.* 1983; **55**: 65.

15. Piermarini, G.J., Block, S., Barnett, J.D. Hydrostatic Limits in Liquids and Solids to 100 kbar. *J. Appl. Phys.* 1973; **44**: 5377.

16. Mao, H.K., Bell, P.M., Shaner, J.W., Steinberg, D.J. Specific Volume Measurements of Cu, Mo, Pd, and Ag and Calibration of the Ruby $R_1$ Fluorescence Pressure Gauge from 0.06 to 1 Mbar. *J. Appl Phys.* 1978; **49**: 3276.

17. Wolford, D.J., Bradley, J.A. Pressure Dependence of Shallow Bound States in Gallium Arsenide. *Solid State Commun.* 1985; **53**: 1069.

Date Received: October 23, 1992

Date Accepted: November 27, 1992