

# Low temperature internal friction of diamond-like carbon films

Xiao Liu <sup>a,1</sup>, D. M. Photiadis <sup>b</sup>, J. A. Bucaro <sup>b</sup>, J. F. Vignola <sup>b</sup>, B. H. Houston <sup>b</sup>,  
Huey-Daw Wu <sup>a</sup>, D. B. Chrisey <sup>b</sup>

<sup>a</sup>*SFA, Inc., Largo, MD 20774, U.S.A.*

<sup>b</sup>*Naval Research Laboratory, Washington DC, 20375, U.S.A.*

---

## Abstract

We have studied the internal friction of amorphous diamond-like carbon films prepared by pulsed-laser deposition from 0.4 to 300 K. The low temperature internal friction below 10 K is dominated by the atomic tunnelling states for amorphous solids, which is a measure of structure disorder. We have tried to vary the content of  $sp^3$  carbon atoms versus  $sp^2$  ones by changing laser fluence, by doping with N and Ar, and by annealing at 500°C for 20 minutes. Our results show that the internal friction varies about one order of magnitude from  $2 \times 10^{-5}$  to  $2 \times 10^{-4}$ , and its value is higher with higher  $sp^3$  content when the film quality is generally considered superior. However, it is known that as-deposited diamond-like carbon films with high  $sp^3$  content are heavily stressed. Annealing and doping are used to release the stress. We conclude that in addition to tetrahedral bonding, low stress is also important in reducing structure disorder associated with the low energy tunnelling states in amorphous solids.

*Keywords:* internal friction, diamond-like carbon, double-paddle oscillator, tunnelling states, internal stress

---

## 1. Introduction

Amorphous diamond-like carbon (DLC) films have the unique combination of properties, such as high values of hardness, elastic moduli, electrical resistivity, and chemical inertness. These properties have stimulated considerable research and development interests for their applications in recent years. The key success that leads to the superior properties of DLC is the ability to prepare films with high content of  $sp^3$  atoms over the  $sp^2$  and with low internal stress [1,2].

After having studied a variety of amorphous silicon (*a*-Si) and amorphous germanium (*a*-Ge) films,

we have reached the conclusion that tetrahedral bonding is an important factor in reducing atomic tunnelling states (TS) in *a*-Si and *a*-Ge films at low temperatures [3]. In certain hydrogenated *a*-Si film, TS can be made to disappear completely [4], which, we believe, is at least partially related to the low internal stress in the material [5]. The existence of low energy TS in all amorphous solids, with the exception mentioned above, is an unsolved mystery in condensed matter physics. For a recent review, see ref. [6]. A systematic internal friction study of DLC prepared by pulsed laser deposition will be a valuable import to understand TS. At the same time, internal friction result may provide useful information about structure disorder in the

---

<sup>1</sup> Corresponding author. E-mail: xliu@genah.nrl.navy.mil

# Report Documentation Page

*Form Approved  
OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>2002</b>	2. REPORT TYPE	3. DATES COVERED <b>00-00-2002 to 00-00-2002</b>	
4. TITLE AND SUBTITLE <b>Low temperature internal friction of diamond-like carbon films</b>		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC, 20375</b>		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>			
13. SUPPLEMENTARY NOTES			
14. ABSTRACT			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>	
			18. NUMBER OF PAGES <b>5</b>
			19a. NAME OF RESPONSIBLE PERSON

Table 1

Some relevant parameters of the DLC films studied in this work.  $Q_0^{-1}$  is the low temperature internal friction plateau explained in text.

Samples	laser fluence (J/cm <sup>2</sup> )	deposition pressure (Torr)	film thickness (nm)	$Q_0^{-1}$ at $T < 10$ K
high f	8.6	$2.6 \times 10^{-5}$	70	$1.2 \times 10^{-4}$
high f:Ar	8.6	Ar: $5 \times 10^{-2}$	230	$7.7 \times 10^{-5}$
low f	4.3	$1.6 \times 10^{-5}$	150	$6.3 \times 10^{-5}$
low f, annealed <sup>a</sup>	4.3	$1.6 \times 10^{-5}$	130	$3.8 \times 10^{-5}$
low f:N	4.4	N <sub>2</sub> : $6 \times 10^{-2}$	400	$2.3 \times 10^{-5}$

<sup>a</sup> At 500°C for 20 minutes.

material, in particular, its dependence on annealing, doping, and laser energy.

## 2. Measurements and results

Samples of DLC films were prepared by pulsed-laser deposition (PLD) technique [7] with a Lambda Physik Kr-F Excimer Laser (wavelength 248 nm, pulse duration 15 ns, repetition rate 10 Hz). Deposition was done in a vacuum chamber with base pressure of  $\sim 2 \times 10^{-5}$  Torr. Target was high purity graphite. Total of 5 samples were studied in this work. We varied laser fluences from 4.3  $\sim$  8.6 J/cm<sup>2</sup>. It crosses the threshold fluence of 5 J/cm<sup>2</sup> at which the structure changes from mostly disordered graphitic to tetrahedral amorphous carbon [2]. For one of the low fluence films we subsequently annealed it at 500°C for 20 minutes in Ar atmosphere in order to observe the effect of stress releasing upon annealing. We also deposited films in partial pressure of Ar and N<sub>2</sub> for doping purpose. The samples were listed in Table 1 with relevant films parameters.

Measurements of internal friction were performed using the double-paddle oscillator (DPO) technique [8]. The oscillators were fabricated out of high purity undoped silicon wafers, with resistivity  $> 5$  kΩcm. The overall dimension of the oscillators was 28 mm high, 20 mm wide, and 0.3 mm thick. The so-called second antisymmetric

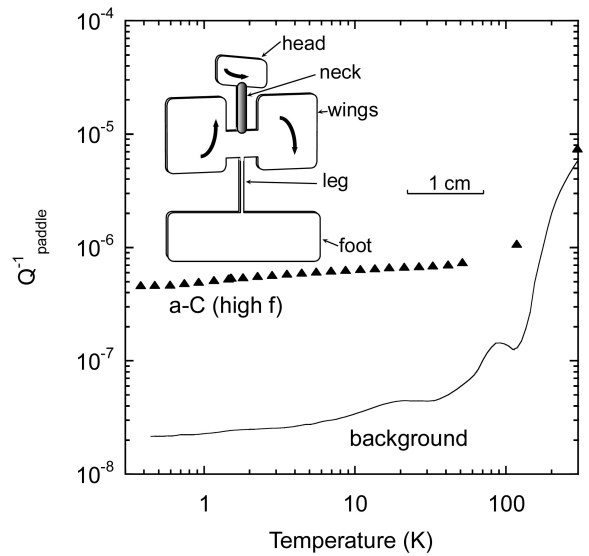


Fig. 1. Internal friction of the double-paddle oscillator  $Q_{osc}^{-1}$  vs. temperature. Shown is the internal friction of the bare paddle oscillator (background) and a paddle oscillator with a 70 nm DLC films deposited in vacuum. The inset is the geometry and illustrated mode shape of the second antisymmetric mode of double-paddle oscillator.

mode had an exceptionally small internal friction  $Q^{-1} \sim 2 \times 10^{-8}$  at low temperatures ( $T < 10$  K), see Fig. 1, which was reproducible within 10% for different oscillators. The small  $Q^{-1}$  was attributed to its unique design. For the second antisymmetric mode, the head and wings vibrated against each other, which led to the torsional oscillation of the neck while leaving the leg and foot with little vibration to minimize the external loss (see the inset of Fig. 1). The film to be studied was deposited onto the neck (shaded area in the inset of Fig. 1). The resonance was excited capacitively at a frequency of 5500 Hz. For details of the internal friction measurements technique, see ref. [9]. The internal friction results presented in this work were obtained exclusively using this mode for maximum detection sensitivity.

Deposition of a thin film onto the oscillator changes its internal friction,  $Q_{osc}^{-1}$ . From the increase above the bare oscillator (substrate) internal friction,  $Q_{sub}^{-1}$ , the internal friction of the thin film itself,  $Q_{film}^{-1}$ , can be calculated through [8]

$$Q_{\text{film}}^{-1} = \frac{G_{\text{sub}} t_{\text{sub}}}{3G_{\text{film}} t_{\text{film}}} (Q_{\text{osc}}^{-1} - Q_{\text{sub}}^{-1}), \quad (1)$$

where  $t$  and  $G$  are thicknesses and shear moduli of substrate and film, respectively.  $G_{\text{sub}} = 6.2 \times 10^{11} \text{ dyn/cm}^{-2}$  is the shear modulus of silicon along  $\langle 110 \rangle$  orientation as for the neck of the DPO. For our DLC films, we use  $G_{\text{film}} = 3.4 \times 10^{12} \text{ dyne/cm}^{-2}$ , which was taken from literature [10]. It was measured by surface Brillouin scattering on samples deposited by the filtered cathodic vacuum arc technique. We understand that the elastic constants of our DLC films may be different from that of the literature, and it may even vary from sample to sample. Because of the complexity of getting the elastic constants measured correctly [10], we have to ignore that for now before more studies of the elastic properties become available.

In Fig. 1, the internal friction of the DPO with and without a DLC film are shown. Deposition of a 70 nm DLC film increases the internal friction by more than one order of magnitude from its background. With eq. 1,  $Q_{\text{film}}^{-1}$  can be calculated, which are shown in Fig. 2 for all five samples studied. Note the background was measured on a different oscillator, which is not a problem due to the excellent reproducibility of the measurement. From above 10 K to 300 K,  $Q_{\text{film}}^{-1}$  exhibits strong temperature dependence. Except for the low fluence and annealed film (labelled ‘low f, annealed’ in Fig. 2),  $Q_{\text{film}}^{-1}$  increases with temperature to a value around  $5 \times 10^{-4}$ , which is almost the same for all the four as-deposited samples, independent of their lower temperature behavior. For the low fluence and annealed film, a maximum is developed at about 190 K while the room temperature internal friction is by one order of magnitude smaller. The decrease of the room temperature internal friction is consistent with the fact that annealing recovers some of the as-grown defects and reduces the internal stress of the film [11]. The internal friction of the as-deposited films above 10 K may be related a thermally activated energy dissipation process that develops a maximum at above room temperature, similar to what has been found in other amorphous solids, see the internal friction of  $a\text{-SiO}_2$  in Fig. 2

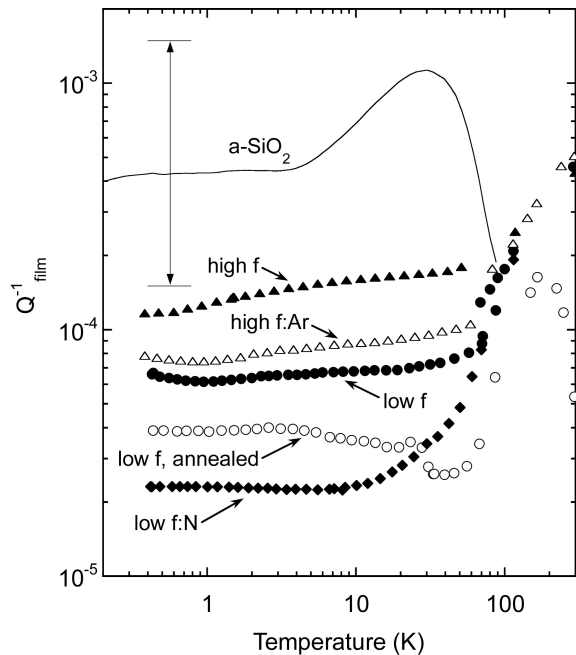


Fig. 2. Internal friction of the amorphous diamond-like carbon films  $Q_{\text{film}}^{-1}$  vs. temperature. The internal friction of bulk  $a\text{-SiO}_2$  is shown for comparison. The double-arrow denotes the ‘glassy range’ explained in text.

and ref. [12]. The annealing may have shifted the maximum to lower temperature.

Below 10 K, the internal friction of all samples is flat in temperature and varies from  $2 \times 10^{-5}$  to  $2 \times 10^{-4}$ . This is a characteristic feature of amorphous solids, and is a direct consequence of elastic energy dissipation by TS due to the broad distribution of their density of states. The flat internal friction is called the internal friction plateau  $Q_0^{-1}$ . According to the model of two-level tunnelling systems (TLS) [13,14] and its implementation [15], which provides a phenomenological description of the observed low temperature thermal and elastic properties of amorphous solids,

$$Q_0^{-1} = \frac{\pi \bar{P} \gamma_i^2}{2 \rho v^2}, \quad (2)$$

where  $\bar{P}$  is the spectral density of TS,  $\gamma$  their coupling energy to the lattice,  $\rho$  the mass density, and  $v$  the speed of sound (in the case of a torsional oscillation in this paper, it is transverse speed of sound). While this quantity,  $Q_0^{-1}$ , has previously

been shown to be of a nearly universal magnitude from  $1.5 \times 10^{-4}$  to  $1.5 \times 10^{-3}$ , called ‘glassy range’, it has recently been found that it can be reduced several orders of magnitude [4]. The variation of the internal friction plateau only occurs in *a*-Si and to some extent also in *a*-Ge [3]. Amorphous *a*-C belongs to the same system with tetrahedral bonding. In Fig. 2, the low temperature internal friction plateaus of the DLC films are all smaller than the glassy range found in all other amorphous systems, indicated by the double-arrow and the internal friction of *a*-SiO<sub>2</sub>. Film ‘high f’ is right at the bottom of the glassy range, while film ‘low f:N’ is one order of magnitude lower. This result is consistent to our findings in *a*-Si and *a*-Ge.

High laser fluence leads to higher sp<sup>3</sup> content [2]. Based on our findings in *a*-Si and *a*-Ge, that will reduce the density of TS. However, we find  $Q_0^{-1}$  is higher for films with higher fluence. Furthermore, annealing at 500°C for 20 minutes should result in almost complete stress relaxation with the conversion of some fourfold carbon atoms into threefold ones [11]. But, we observe that  $Q_0^{-1}$  decreases after annealing. Our results show that tetrahedral bonding is not the only important parameter that determines the density of TS in systems with fourfold coordination. Just as we have seen in *a*-Si, the film that has smallest low temperature internal friction is the one with minimal internal stress. Doping with Ar or N helps to relax the stress, while they produce more carbon atoms with sp<sup>2</sup> content [16]. This is consistent with the observed reduction of  $Q_0^{-1}$  upon doping, either on high or low fluence.

According to the constraint counting model [17] and its subsequent modification [18], a three dimensional glass is considered rigid with no extra degree of freedom when its average coordination number exceeds 2.4. In this sense, even the threefold coordination in sp<sup>2</sup> carbon atom is sufficient in eliminating the TS. Additional coordination may only cause stress, and hence increased local disorder in heavily stressed region.

### 3. Conclusion

We confirm that *a*-C, just like *a*-Si and *a*-Ge, belongs to the tetrahedrally bonded amorphous system, in which the low temperature internal friction can display a wide variation, deviating from the glassy range established for all other amorphous solids. However, the fourfold atomic bonding is not the decisive parameter in determining the atomic tunnelling states. Rather, the internal stress of the thin film materials is. The nature of the tunnelling states is still to be explored.

### Acknowledgement

This work was supported by the Office of Naval Research.

### References

- [1] T. A. Friedmann, J. P. Sullivan, J. A. Knapp, D. R. Tallant, D. M. Follstaedt, D. L. Medlin, P. B. Mirkarimi, Appl. Phys. Lett. 71 (1997) 3820.
- [2] M. Bonelli, A. P. Fioravanti, A. Miotello, P. M. Ossi, Europhys. Lett. 50 (2000) 501.
- [3] X. Liu, D. M. Photiadis, H. D. Wu, D. B. Chrisey, R. O. Pohl, R. S. Crandall, Philos. Mag. B 82 (2002) 185.
- [4] X. Liu, B. E. White, Jr., R. O. Pohl, E. Iwanizcko, K. M. Jones, A. H. Mahan, B. N. Nelson, R. S. Crandall, S. Veprek, Phys. Rev. Lett. 78 (1997) 4418.
- [5] D. Han, J. Baugh, G. Yue, Q. Wang, Phys. Rev. B, 62(2000) 7169.
- [6] R. O. Pohl, X. Liu, E. Thompson, Rev. Mod. Phys. (in press).
- [7] D. B. Chrisey, G. K. Hubler, Pulsed Laser Deposition of Thin Films, New York, Wiley 1994.
- [8] B. E. White, Jr., R. O. Pohl, Mat. Res. Soc. Symp. Proc. 356 (1995) 567.
- [9] C. L. Spiel, R. O. Pohl, A. T. Zehnder, Rev. Sci. Instrum. 72 (2001) 1482.
- [10] A. C. Ferrari, J. Roberts, M. G. Beghi, C. E. Bottani, R. Ferulano, R. Pastorelli, Appl. Phys. Lett. 75 (1999) 1893.
- [11] J. P. Sullivan, T. A. Friedmann, A. G. Baca, J. Electron. Mater. 26(1997) 1021.

- [12] S. Hunklinger, W. Arnold, in: W. P. Mason, P. G. Klemens (Eds.), *Physical Acoustics*, Academic, New York, 1976, vol. 12, p.155.
- [13] P. W. Anderson, B. I. Halperin, C. M. Varma, *Philos. Mag.* 25 (1972) 1.
- [14] W. A. Phillips, *J. Low Temp. Phys.* 7 (1972) 351.
- [15] J. Jäckle, *Z. Phys. B: Condens. Matter*, 257 (1972) 212.
- [16] T. Szörényi, E. Fogarassy, C. Fuchs, J. Hommet, F. Le Normand, *Appl. Phys. A* 69 (1999) S941.
- [17] J. C. Phillips, *J. Non-Cryst. Solids*, 34 (1979) 153.
- [18] M. F. Thorpe, *J. Non-Cryst. Solids*, 57 (1983) 355.