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Laser fluence dependence of the elastic properties of diamond-like carbon films prepared by pulsed-laser deposition

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Abstract

We studied the temperature dependence of internal friction of variety of amorphous diamond-like carbon films prepared by pulsed-laser deposition. Like the most of amorphous solids, the internal friction below 10 K exhibits a temperature independent plateau, which is caused by the atomic tunnelling states—a measure of structure disorder. In this work, we have varied the concentration of sp^3 versus sp^2 carbon atoms by increasing laser fluence from 1.5 to 30 J/cm^2. Our results show that the internal friction has a nonmonotonic dependence on sp^3/sp^2 ratio with the values of the internal friction plateaus varying between 6×10^{-5} and 1.1×10^{-4}. We explain our findings as a result of a possible competition between the increase of atomic bonding and the increase of internal strain in the films, both of which are important in determining the tunneling states in amorphous solids. The importance of the internal strain in diamond-like carbon films is consistent with our previous study on laser fluence, doping, and annealing, which we will review as well. In contrast, no significant dependence of laser fluence is found in shear moduli of the films, which vary between 220 and 250 GPa.

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Keywords: Internal friction; Diamond-like carbon; Double-paddle oscillator; Tunnelling states; Internal strain

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 films is the ability to prepare films with high content of sp^3 atoms over the sp^2 and with low internal strain [1,2]. Hydrogen free DLC films can be prepared by techniques like, filtered arc discharge [3], pulsed-laser deposition [1], sputtering [4], and ion beam assisted deposition [5]. The elastic properties of these thin film materials are not only technically important [6–10], but also interesting to understanding of the relationship between the number of covalent bonding and structure disorder in dielectric thin films [11,12].

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 in *a*-Si and *a*-Ge films at low temperatures [11]. In certain hydrogenated *a*-Si film, atomic tunnelling states can be made to disappear completely [13], which, we believe, is at least partially related to the low internal strain in the material [14]. The existence of low energy tunnelling states in all amorphous solids, with the exception mentioned above, is an unsolved mystery in condensed matter physics. For a recent review, see Ref. [15]. In this work, we systematically study the temperature dependence of internal friction, Q^{-1}, of DLC films prepared by pulsed-laser deposition (PLD). The internal friction is a sensitive measure of structural disorder and defects in solids, defined as

$$Q^{-1} = \frac{\Delta E}{2\pi E}, \quad (1)$$

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where $\Delta E/E$ is the fraction of energy loss per cycle of periodic fluctuating stress field due to anelastic behavior. We vary the laser fluence so that we can control the sp^3 and sp^2 concentrations in the films to modify the mean coordination number between $m = 3$ and 4. Our results suggest an interplay between atomic bonding and internal strain. This result support our previous study [12] in which we found that the internal strain is an important parameter in determining the structural disorder in DLC films.

2. Experimental

The films were deposited at the University of Trento at laser fluences ranging between 1.5 to 30 J/cm^2, using highly oriented pyrolitic graphite as target [16]. The laser source was a KrF excimer laser of 248 nm wavelength, 20 ns pulse duration, and 10 Hz repetition rate. In these experiments the deposition chamber was evacuated to reach pressures lower than 2×10^{-4} Pa before laser irradiation. The target-to-substrate distance was fixed at 70 mm. The film deposition parameters have been chosen in such a way that films would be deposited with appropriate atomic coordination, as carefully investigated in the Trento laboratory [2,17,18]. Table 1 lists some of the film deposition parameters. According to Refs. [2,17], the sp^3 concentration would vary from 40 to 80%, as measured on similarly prepared films. The film thicknesses were determined by a Alpha step profilometer.

Measurements of internal friction were performed using the double-paddle oscillator (DPO) technique [19]. The DPOs were fabricated out of high purity P doped silicon wafers, which were $\langle 1\,0\,0\rangle$ oriented and had resistivities >5 kΩ cm. The overall dimension of a DPO is 28 mm high, 20 mm wide, and 0.3 mm thick; see Fig. 1. The DPO consists of a head, a neck, two wings, a leg, and a foot. The main axes are along the $\langle 1\,1\,0\rangle$ orientation. On the back of the DPO a metal film (30 Å Cr and 500 Å Au) was deposited from the foot up to the wings but not on the neck and the head. The DPO was then clamped to an invar block using invar screws and a precision torque wrench. This minimized the effect of thermal contraction during cool down and ensured reproducibility after repeated remounting of the same DPO. Two electrodes were coupled to the wings from the back side so that the DPO could be driven and detected capacitively. For our internal friction measurements, we used the so-called second antisymmetric mode oscillating at ~5500 Hz. It has an exceptionally small background internal friction $Q^{-1} \approx 2 \times 10^{-8}$ at low temperatures ($T < 10$ K) which is reproducible within ±10% for different DPOs. The small Q^{-1} is attributed to its unique design and mode shape. During oscillation, the head and the wings vibrate against each other, which leads to a torsional oscillation of the neck while leaving the leg and the foot with little vibration, minimizing the external loss. The film to be studied was deposited onto the neck (hatched area in Fig. 1). The internal friction results presented in this work were obtained exclusively using this mode for maximum detection sensitivity.

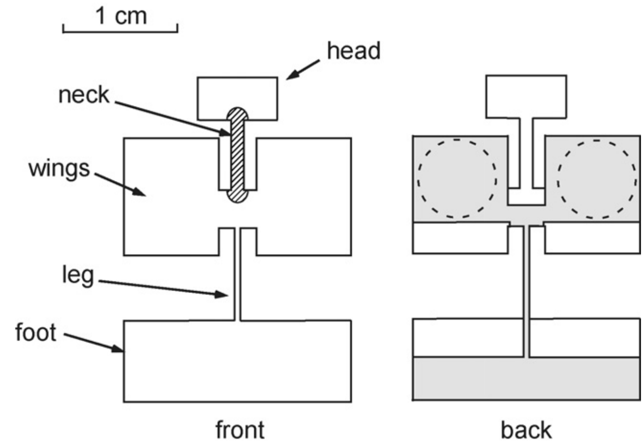

Fig. 1. Outline of the double-paddle oscillator. The left side shows the front view, and the right side shows the back view. The hatched area in the front view is the amorphous diamond-like carbon film deposited through a stainless steel mask. On the back side of the paddle a thin Cr and Au film is covered in the gray area. The dashed circles indicate the position of electrodes for capacitive drive and detection.

Deposition of a thin film onto the DPO changes its internal friction, Q^{-1}_{osc}, as well as its resonance frequency, f_{osc}, from those of a bare DPO, Q^{-1}_{sub} and f_{sub}, respectively. From the difference, the shear modulus and the internal friction of the film can be calculated through

$$Q^{-1}_{film} = \frac{G_{sub} t_{sub}}{3 G_{film} t_{film}} (Q^{-1}_{osc} - Q^{-1}_{sub}) + Q^{-1}_{osc}, \qquad (2)$$

$$\frac{f_{osc} - f_{sub}}{f_{sub}} = \frac{t_{film}}{2 t_{sub}} \left[\frac{3 G_{film}}{G_{sub}} - \frac{\rho_{film}}{\rho_{sub}} (1+\eta)^{-1} \right], \qquad (3)$$

where t, ρ, and G are thicknesses, mass densities, and shear moduli of substrate and film, respectively; η is the ratio of moments of inertia of the uncoated versus the coated part of head and neck (see Fig. 1). We include here a correction term in Eq. (2), so that it will be valid even if Q^{-1}_{film} is comparable to Q^{-1}_{sub}

Table 1
Laser fluence, number of pulses, film thickness, room temperature shear modulus, and internal friction at 1 K are listed below

Fluences (J/cm^2)	Pulses ($\times 10^3$)	Thickness (nm)	G_{film} (GPa)	Q_0^{-1} ($T = 1$ K) ($\times 10^{-4}$)
30	20	142	226	0.86
26	22	155	223	1.00
18	25	200	244	1.32
10	25	221	254	1.42
5	18	156	220	1.19
1.5	50	209	252	0.80