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Is stress necessary to stabilise sp^3 bonding in diamond-like carbon?

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Abstract

The role of compressive stress in producing sp^3 bonding in diamond-like carbon is of interest both technologically and scientifically. Stress limits the maximum thickness of adherent films, and it is desired to produce much thicker films for protective coatings and for making micro-electromechanical systems. Stress is important theoretically, because it is often linked to the deposition process. A strong correlation between macroscopic stress and sp^3 fraction in diamond-like carbons has been noted, particularly for tetrahedral amorphous carbon (ta-C). However, a survey of data shows that a given stress produces films with sp^3 contents between 20 and 85%, while for a given sp^3 content, stresses between 2 and 19 GPa have been found. We propose that the main cause of stress is ion bombardment, and that a low energy of only 20 eV/ion is needed to produce films with an sp^3 content over 70%. We discuss the various models linking stress and the sp^3 fraction in ta-C. The role of densification vs. compressive stress in stabilising sp^3 bonding is also discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Diamond-like carbon; Stress; Tetrahedral amorphous carbon; sp^3 bonding

1. Introduction

The past 10 years have seen considerable work on tetrahedral amorphous carbon (ta-C), hydrogen-free, highly sp^3 form of diamond-like carbon. Ta-C can be deposited by various methods such as mass selected ion beams (MSIB) [1], pulsed laser deposition (PLD) [2], magnetron sputtering with ion plating [3] or by filtered cathodic vacuum arc (FCVA) [4–6]. Ta-C has a much better thermal stability than a-C:H, largely because it does not contain hydrogen [4–10]. Under vacuum, the bulk sp^3 to sp^2 transition happens only above 1100 °C [11]. In addition, ta-C possesses extraordinary mechanical properties: Young's modulus, $E \sim 760$ GPa [12,13], Bulk modulus, $B \sim 330$ GPa [12], shear modulus, $G \sim 340$ GPa [12], and hardness ~ 80 GPa [9,14,15]. These are much superior to those of most a-C:Hs, because of its higher C–C sp^3 content, up to 90% [16]. Its optical gap can reach nearly 4 eV [17]. Ta–C also has a low friction coefficient, decreasing with higher humidity [18].

After an enthusiastic start towards various electronic and mechanical applications, the development was inhibited by three major problems. (1) the high defect density hampering the electronic applications [19,20]; (2) the realisation that the field emission properties were due to the field enhancement on 'spurious' sp^2 clusters or extrinsic particles [21], so that carbon nanotubes appear better candidates; and (3) the high compressive stress, generally limiting the maximum thickness to ~ 100 nm [5,15]. Recently, the interest in applications of ta-C has been revived due to the possibility of overcoming the stress problem [9,11,22,23], and also by the increasing need of ultra-thin films for hard disk coating [24,25], where stress is not an issue. Furthermore, it was shown that the defects in ta-C can be engineered, reducing their number but keeping a significant optical gap [17], and that ta-C films can be formed into efficient field emission structures [26].

A prospective application of ta-C is in Micro-Electro-Mechanical-Systems (MEMS), due to its superior wear-resistant qualities, low stiction (i.e. a combination of stickiness and friction), and potential as a biocompatible material. Indeed, Sandia made several MEMS structures with ta-C, such as an electrostatically activated comb drive [27,28], from thick, stress-free ta-C films produced by post-deposition annealing. The high stiffness of ta-C [12] could also be exploited in GHz surface acoustic wave devices. A major advantage of ta-C over polycrystalline diamond is the room-temperature deposition

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process, allowing the coating of a much wider range of substrates, and the atomic smoothness. More generally, ta-C and diamond-like carbons (DLC) are viable materials for wear-resistant applications on cutting tools, automotive components, orthopaedic prostheses, protective and UV absorbing coating on glasses and optical components [29].

These 'bulk' applications need stress-free ta-C films. It is, however, possible to grow thick ($\sim$6 μm), well-adherent and highly stressed films by creating a strong substrate–film interface by a high bias pulse preceding the deposition [29]. Various strategies to reduce the stress in as-deposited DLC films have been proposed, such as incorporating metals [30], silicon [31], boron [32] or multi-layers [33] or post-deposition annealing [9,11,22,23]. But the real issue is if stress is necessary to stabilise the sp^3 bonding [34].

In this paper, we critically assess the origin of stress in ta-C and show how the usually quoted stress vs. sp^3 relations are an unfortunate consequence of the existing deposition procedures [3,35–37]. The main conclusion is that macroscopic stress is not necessary to produce a high sp^3 content.

2. Stress vs. post-deposition annealing and high temperature deposition of ta-C

The stress-release by annealing [9,11,22,23] clearly show that a ta-C film can exist with no macroscopic stress. We noted previously [11] that while stress may be necessary to stabilise the sp^3 phase during deposition, once the sp^3 phase is formed, it is no longer needed for stabilisation and so stress can be released without any appreciable structural change. A simple model was proposed to account for the stress relief, based on the rearrangement of the sp^2 sites, requiring, little, if any, sp^3 to sp^2 conversion, in accordance with experiments [11].

While the atomic volume of an sp^2 site exceeds that of an sp^3 site, its in-plane size is less, due to its shorter bond length [22,23]. Thus, the formation of sp^2 sites with their σ plane aligned in the plane of compression will relieve a biaxial compressive stress. The changes in stress and strain in a thin film under biaxial stress are related by [38]: $\Delta\sigma = E/(1-\nu)\Delta\varepsilon$, where $\Delta\sigma$ is the stress variation, and $\Delta\varepsilon$ is the strain variation. We have neglected any variations in elastic constants and attributed all the stress relief to strain variation. Taking the change in film stress as $\Delta\sigma\sim 10$ GPa and $E/(1-\nu)\sim 870$ GPa [12], the required $\Delta\varepsilon$ is $\sim$1.2%. Thus, only a small strain is needed to relieve stress. This can be accounted by a slight decrease in the density or by a small relaxation of the structure. Siegal et al. [39] observed a $\sim$7% density reduction for PLD ta-C samples annealed at $\sim$600 °C, the temperature of total stress relief.

If we attribute the strain change to a decrease in sp^3 fraction, the fraction of sp^2 sites needed is $\Delta n\sim 12\%$, given that $\varepsilon\sim\Delta n\cdot\Delta r$, with the bond length change $\Delta r\sim 10\%$ for every sp^3 to sp^2 conversion. On the other hand, the same $\Delta\varepsilon$ can be achieved by rearranging existing sp^2 sites, so there is less need for sp^3 to sp^2 conversion. A confirmation of this preferential orientation of the sp^2 phase was derived by anisotropy analysis of the EELS K-edge [40] and by comparing parallel and perpendicular conductivity measurements [41]. Further evidence of the movement of sp^2 sites, for a fixed sp^3 content, comes from fluctuation microscopy [42] and a combination of ESR and optical measurements [17], which show an increased ordering of sp^2 sites with a reduction of the dihedral angle between π electrons. Thus, there is experimental evidence that the required small strain variation is mainly due to some rearrangement of the sp^2 sites, accompanied by a very small, if any, sp^3 to sp^2 conversion. The clustering of the sp^2 phase for a fixed sp^3 content was also found during high temperature deposition of ta-C [43], and is indeed a common feature in amorphous and disordered carbons [44]. A comparison of the two processes can thus lead to further insights in the stress relaxation problem.

The high thermal stability of ta-C after deposition (> 1100 °C) contrasts with the much lower transition temperature to sp^2 bonding found during deposition itself, of approximately 250 °C [43,45]. This implies that the relaxation processes during and after deposition have significant differences. However, the optical gap, in-plane resistivity and intensity ratio of the Raman D and G bands, $I(D)/I(G)$, are observed to decrease gradually just above room temperature [43,45], similar to that seen for post-deposition annealing at 700 °C $< T <$ 1100 °C [11,46]. The $I(D)/I(G)$ ratio is a measure of sp^2 clustering [44]. The ability of the sp^2 sites to condense into larger clusters, at constant sp^3 fraction, indicates that the sp^2 sites act like defects in the sp^3 matrix and can diffuse within it. It also means that the sp^2 sites diffuse at lower energy than that required for the conversion of sp^3 sites to sp^2 sites. This accounts for the lower annealing temperature of sp^2 rich a-C than of sp^3 rich ta-C [7,8,47]. Another consequence is that above the transition temperature, the newly formed sp^2 sites will also condense into clusters to the same degree as the existing sp^2 sites. Thus, the newly formed sp^2 sites cluster in the same way since their diffusion energy is less than the conversion energy.

Estimates of the activation energies for (1) sp^2 clustering, and (2) sp^3 to sp^2 conversion in annealing and in high temperature deposition were extracted from the Arrhenius plot of $I(D)/I(G)$ for process (1) Fig. 1, and $kT\ln(\nu\tau)$ for process (2) since this is a sharp transition not allowing a proper Arrhenius plot. We assumed $\nu\tau\sim 5\times 10^{13}$, using a typical phonon frequency of $\nu\sim 5\times 10^{13}$ s^{-1} and an experimental time $\tau\sim 1$ s. We

found that the activation energy for sp^2 clustering for high temperature depositions is $\sim$0.2 eV, Fig. 1b, and for sp^2 clustering for post deposition annealing is $\sim$0.28 eV, Fig. 1a. On the other hand, for bulk $sp^3 \rightarrow sp^2$ conversion, we get $\sim$1.2 eV for high temperature deposition and $\sim$3.3 eV for post-deposition annealing. The activation energy for stress release is found to be $\sim$0.12 eV, Fig. 1c.

These estimates suggest that the stress reduction is initiated by bond length and angle relaxation within the sp^2 phase, before $sp^3 \rightarrow sp^2$ conversion. Indeed, we noted above that if a stress reduction was due solely to $sp^3 \rightarrow sp^2$ conversion, this would require a reduction in the sp^3 fraction $\Delta n \sim 12\%$, which is not observed experimentally [11]. However, despite the parallels between high temperature deposition and post-deposition annealing experiments, there is a major difference: for high temperature deposition the stress relaxation only happens at the bulk sp^3 to sp^2 conversion [45]. This is a key factor to understand the reason for stress build-up, as we discuss in the next section.

3. Stress vs. sp^3 content: what do the deposition models tell us and what is the real stress vs. sp^3 relation?

The stress is generally considered to be an intrinsic property of DLC films arising from the deposition mechanism creating the sp^3 bonds. Indeed, since the first reports of ta-C [35] this idea became wide spread in the DLC community; high stress means high sp^3 and vice-versa, so high stresses are needed for high sp^3. But what is the view given by the current deposition models?

The picture of McKenzie [4,35,36] considers that the compressive stress, from ion bombardment, causes the formation of sp^3 sites. The central part of this model is a phase transition from an sp^2-rich to an sp^3-rich phase at a critical value of compressive stress, which stabilises the sp^3 bonding. This idea is related to the graphite–diamond transition in the pressure–temperature phase diagram of carbon. Indeed, McKenzie et al. [36] still claim that a non-linear relation between stress and sp^3 exists, with a threshold stress of $\sim$4 GPa for a rapid increase in the sp^3 fraction. Other authors presented a linear relation of stress and sp^3 [15].

A popular model to explain the formation and dependence of compressive stress on incident ion energy is by Davis [48]. Often his model is considered to be explaining also the sp^3 formation, due to the belief that stress is synonymous of sp^3. However, a closer look at this model shows that it is effectively an *elastic model* only explaining the stress generation in a slab, where an increasing number of atoms is implanted, thus causing its bending. Indeed, a fixed Young's modulus and Poisson's ratio are used [48], which are not consistent with a change in the sp^3, which directly correlates with the elastic constants [12]. This model, however, clearly explains why, for an almost fixed sp^3 content, an increasing ion flux and energy causes an increasing stress.

Another model, superficially similar to that of Davis, is due to Robertson [49]. In this case, the sp^3 bonding is directly related to the densification produced by subplantation. This model is thus plastic, and links sp^3 and density. Indeed, by means of XRR and EELS we could fit a linear relation between sp^3 content and density [40]. However, due to the similarity of the formula of Robertson, describing the density evolution vs. ion energy and flux, and that of Davis, it has been often interpreted that this model also supports the idea that the density increase corresponds to a stress increase. However, Robertson's model is *plastic*, so it allows, in principle, the relaxation mechanisms leading to zero stress films.

The subplantation model of Lifshitz et al. [50] or Hofsass et al. [51] do not deal with stress during deposition and are *plastic* models, so allowing for zero stress films.

Tamor [34] already noted that a purely thermodynamic picture leads to the conclusion that stress is essential for the very existence of ta-C, and that the kinetic picture [48–51] would imply that stress is just an accident and might be avoided. To cut through this 'chicken or egg' question, he considered a *gedanken*

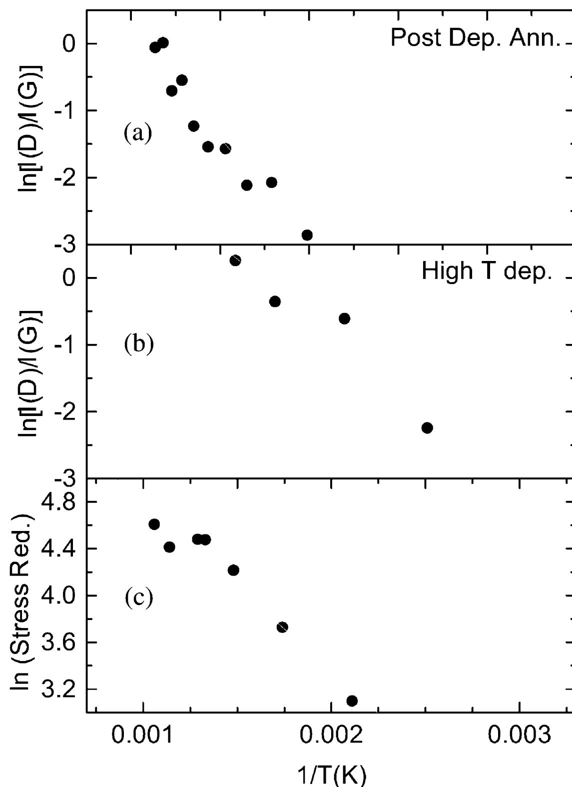

Fig. 1. Arrhenius plots of (a) $I(D)/I(G)$ for post-deposition annealing of ta-C [11]; (b) $I(D)/I(G)$ for high temperature deposition of ta-C [43]; and (c) stress reduction [11].

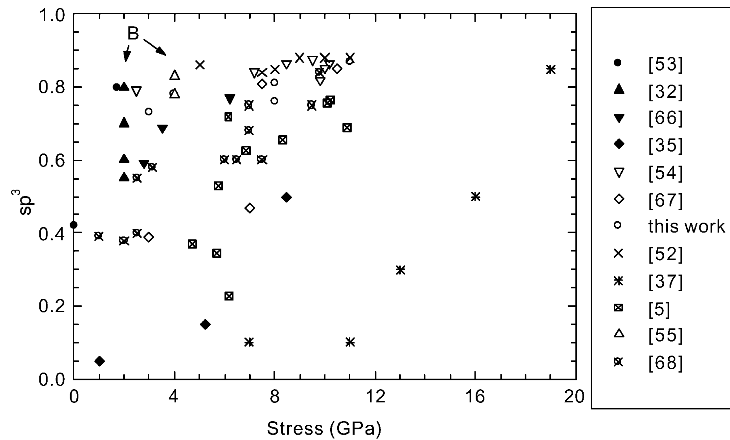

Fig. 2. Collection of stress and sp^3 data from as-deposited ta-C samples found in literature and for a series of films produced in this work with a single bend FCVA. Note how the data are spread in the *x*–*y*-axis with no clear relation stress/sp^3. Data on ta-C:B have also been included [5,32,35,37,52–55,66–68, this work].

experiment, by which he concluded that a even if a 100% sp^3 ta-C could exist, it would 'self-stress' due to a spontaneous conversion of sp^3 to sp^2 to reduce bond angle distortions. The volume of the new sp^2 sites would be larger that the previous sp^3 sites, which would create compressive stress. He thus concluded that stress is unavoidable.

We believe in the fact that stress can be relieved by a tiny strain relaxation clearly suggests that high stress is just an 'accident' of the deposition process. To test this hypothesis, we plotted in Fig. 2 all the available stress vs. sp^3 measurements, with the sp^3 content directly measured by EELS. These data clearly show that there is no correlation between stress and sp^3 fraction in as-deposited samples. In fact, for a given stress, films with sp^3 content between 20 and 80% have been produced and for a given sp^3 content, stresses between 2 and 19 GPa have been measured.

A careful examination of the data of Fig. 2 implies that the main cause of stress is the ion bombardment, but only a low energy (not higher than 20 eV/atom) is necessary to produce films with sp^3 contents higher than 70%. The further increase in energy is mainly increasing the stress, without an appreciable increase in sp^3 (and an extreme increase of ion energy leads again to graphitisation and low stress). This can be deduced by comparing the deposition conditions of the low- and high-stress data. Indeed, in our S-bend FCVA, a 300% lower stress for a fixed sp^3 content can be achieved without any doping or annealing, by depositing films at a floating potential (20 eV ion energy) instead of −100-V bias [52]. The *x* data in Fig. 2 represent a series of these films deposited for increasing ion energy, and they show the stress increasing from ~4 to 12 GPa, with a fixed sp^3. Furthermore, 1.7–2.5-GPa stress, 80% sp^3 ta-C films have been reported by Bonelli et al. [53] and Xu et al. [54]. Fig. 2 also plots data for two series of ta-C:B films [32,55]. The samples of Kleinsorge et al. [55] have a higher stress than those of Chhowalla et al. [32], but have the same B content. This shows that boron itself is not the main cause of stress reduction.

The data of Schwan et al. [3,37] deserve particular attention. They use magnetron sputtering with ion plating to deposit a-Cs. In this case, the film forming particles are low energy neutral carbon atoms (sputtered from a graphite target) and the necessary momentum for densification of the film is provided by incident argon ions. Not surprisingly, they produce very high stress (13 GPa) very low sp^3 (~20%) and density (2.1 g/cm^3) films, before the Ar ion plating can lead to significant densification and thus a sp^3 increase (but also huge stresses of 19–20 GPa). A similar effect is also seen by Lacerda et al. [56], who clearly showed that the stress up to 12 GPa does not necessarily create high sp^3 films. In this case, a low-energy carbon beam was assisted by Ne, Ar or Kr beams of increasing ion energy.

Further evidence that the ion bombardment is the main cause of stress comes from comparing high-temperature deposition and post-deposition annealing of ta-C, as in Section 2. High temperature depositions and post-deposition annealing lead to similar phenomena, with clustering of the sp^2 phase and decreasing gap, resistivity and increasing $I(D)/I(G)$ *before* the sharp drop in the sp^3 content. However, in the case of high temperature depositions the stress *does not* decrease until the sharp drop in sp^3 content [45]. Resistivity measurements and anisotropy analysis of EELS K edge and HRTEM [40,41,57,58] show a preferential orientation of the sp^2 phase with the *c*-axis parallel to the Si substrate for samples deposited at high temperatures, and vice-versa for samples annealed after deposition [40,41].

McKenzie et al. [58–60] suggested that the preferential alignment with the *c*-axis parallel to the Si substrate is due to the biaxial stress in the subplanted films, favouring the formation of graphitic layers, so that the stress is normal to the compressible planes (basal planes). McCarty [61], however, showed that this thermodynamic argument of McKenzie and Bilek [59,60] is unsound and that the Gibbs free energy is *not* minimised for the experimentally observed orientation. This means that preferential orientation is mainly due to the preferential displacement of carbon atoms perpendicular to the σ bond plane, not stress. This is due to the anisotropy of ion displacements in graphite, being easier along the *c*-axis [62]. This can then explain the stress build-up for films deposited at high temperature. Graphitic clusters with *c*-axis parallel to the Si substrate do not lead to a minimum free energy and thus minimum stress [61], even though when the $sp^3 \rightarrow sp^2$ transition happens, the stress also decreases due to the squeezing of the layers. For post-deposition annealed films, where there is no ion bombardment, the sp^2 sites tend to align with the substrate, contributing to a stress reduction.

Recently, Kelires [63,64] re-examined his early simulations of atomic level stresses. The starting point is the observation that the stress generation is a local process extending over a few atomic volumes, just as subplantation events are. Therefore, what really matters is the local character of the stress tensor. He found that compressive local stresses favour the formation of the sp^3 sites, while tensile stresses favour sp^2 sites. Indeed sp^3 sites are on the average under compressive stress and the sp^2 sites under tensile stress. However, the macroscopic average (intrinsic) stress of the relaxed ta-C film corresponds to zero total stress. He thus explained the stress relief in post-deposition annealing as a structural relaxation of bond length and angles to optimum values, even without conversion of sp^3 sites. This agrees with our model discussed earlier [11]. Kelires [63,64] proposes that the high stress usually observed for as-deposited films arises as stressed non-equilibrium local structures are frozen-in during deposition. The as-deposited network does not have enough energy to overcome the potential barrier to the stress-free relaxed structure.

A trick in order to allow this relaxation was devised by Anttila et al. [65]. They coated the Si substrate with a thick soft metal (e.g. Al and Cu [65]), on which the ta-C can 'flow' and relax. This technique also involves the deposition of a very thin (~100 nm) layer of a carbide forming metal (Ti or Ta) on the top of the soft substrate to ensure suitable adhesion [29,65]. This allowed the growth of several microns thick as-deposited ta-C films. It is possible that in order to easily achieve stress-free ta-C films, it will be necessary to do away with reaching the highest sp^3 content of ~90%. However, the advantage of having stress-free film will compensate for the small loss in mechanical properties of 70–80% sp^3 films [12].

4. Conclusions

We critically reviewed the annealing experiments leading to stress release for ta-C films. We showed that the reason for stress release is a rearrangement within the sp^2 phase. The main cause of stress build-up in ta-C films is ion bombardment, however, macroscopic stress is not necessary to stabilise the sp^3 phase. We showed how no experimental stress vs. sp^3 relation exists when a wide range of experimental data on various deposition techniques is considered. The sp^3 phase build-up is essentially a 'plastic' mechanism, which does not involve the presence of high stress. Different strategies for the production of stress-free as-deposited ta-C films, with no need of doping or annealing, should be possible.

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