专题——2017 年国家自然科学基金研究进展

元素掺杂类金刚石碳膜降内应力研究综述

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摘　要：我国汽车行业与国际同行的差距主要在于发动机关键零部件的摩擦磨损。类金刚石（DLC）碳膜技术是解决发动机关键零部件摩擦磨损问题的有效途径，但传统的 DLC 碳膜在制备过程中会产生较高的内应力（可达 10GPa）,从而导致薄膜失效。首先分析了 DLC 碳膜在汽车零部件领域的应用背景，探讨了薄膜内应力的来源，重点综述了异质元素掺杂降低类金刚石碳膜内应力的研究现状。常用掺杂元素按化学性质可分为碳化物形成元素与非碳化物形成元素，不同于其他分类方法，笔者按掺杂元素的组元多少进行划分，从单元掺杂、二元或多元掺杂入手，系统分析了各种掺杂方式、掺杂元素的优缺点。在此基础上，指出元素掺杂降低类金刚石碳膜内应力的研究从最初的单一元素掺杂，逐步发展到了二元或多元元素掺杂；从碳化物形成元素掺杂、非碳化物形成元素掺杂，逐步发展到碳化物形成元素与非碳化物形成元素的多元共掺杂；所研究的类金刚石碳膜的显微结构也从最初的非晶态结构向多元、多相结构发展，以期获得良好的综合机械性能。

关键词：内应力；元素掺杂；类金刚石碳膜；纳米复合薄膜；摩擦学性能
中图分类号：TG147　　**文献标识码：**A　　**文章编号：**1001-3660(2018)06-0095-09
DOI：10.16490/j.cnki.issn.1001-3660.2018.06.015

Internal Stress Reduction in Diamond-like Carbon Coatings via Elemental Doping: A Review

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ABSTRACT: Tribological properties of key engine components show the big gap between domestic automotive industry and international counterpart. Diamond-like carbon (DLC) coating technique can effectively over come tribological problem of key engine components. Usually, high internal residual stress (up to 10 GPa) generate din deposition process will lead to failure of pure DLC coatings. Application background of DLC coatings in the field of automotive components was analyzed firstly, origin of internal stress in DLC coatings was discussed, and research status of internal stress reduction in DLC coatings by elemental doping was reviewed emphatically. Common doping elements could be classified into carbide forming elements and non-carbide

收稿日期：2018-03-30；修订日期：2018-05-05
Received：2018-03-30；**Revised**：2018-05-05
基金项目：国家自然科学基金项目（51771037，51671153）；重庆市基础与前沿研究计划项目（cstc2015jcyjA70005）；材料腐蚀与防护四川省重点实验室开放基金（2016CL13）
Fund：Supported by National Natural Science Foundation of China (51771037, 51671153), Fundamental and Advanced Technology of Chongqing (cstc2015jcyjA70005) and Opening Project of Material Corrosion and Protection Key Laboratory of Sichuan Province (2016CL13)
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forming elements on the basis of chemical property. However, the elements in this paper were classified according to constituent elements of doping elements instead of other approaches. Advantages and disadvantages of various doping methods and doping elements were analyzed systematically by starting with single- and multi- element doping. On this basis, it was pointed out that objects of studies on internal stress reduction in DLC coatings by elemental doping developed from single element in the beginning into multi-element doping gradually; and from carbide forming elements and non-carbide forming elements into multi-element co-doping of carbide forming elements and non-carbide forming elements. Microstructure of studied DLC coatings developed from amorphous structure into multi-element and multiphase structures, so as to obtain better comprehensive mechanical properties.

KEY WORDS: internal stress; element doping; diamond-like carbon coatings; nanocomposite thin films; tribological property

中国已经连续 5 年成为全球第一大汽车消费国[1]。新能源汽车可降低石油消耗，但考虑到其偏低的市场占有率及普及速度，仍不足以彻底改变中国车用市场的能源结构。到 2018 年，中国原油对外依存度或超过 70%，汽车节油降耗关乎国家能源安全。基于中国国情，工信部已经推出了严格的油耗评价体系。从 2005 年"第一阶段"燃油限制到 2015 年实施的"第三阶段"，要求整车企业的加权平均油耗不高于 6.9 L/100 km[2]。然而，根据工信部公布的企业平均油耗情况，2013 年，79 家国产车企业的油耗达标率仅为 72%。

降低传统车燃油消耗的主要技术路线有高性能发动机技术、轻量化技术和新能源技术等，其中采用高性能发动机技术有望实现降低 7%～12%的燃料消耗[3]。我国汽车行业与世界同行的差距主要在于发动机关键零部件，各种摩擦副是发动机的关键零部件，包括气门挺柱、气门导管、气门、活塞环、活塞、气缸筒、连杆等。摩擦副的摩擦与磨损问题无处不在，摩擦会消耗发动机 48%的能量；过量磨损导致的零件失效，占发动机总成故障的 42. 7%。

类金刚石（DLC，diamond-like carbon）膜技术是解决汽车摩擦磨损问题的先进表面改性技术，有望使发动机的油耗降低 1%～3%，CO_2 排放降低 2%～4%，寿命提高 2 倍。根据汽车工业协会的统计，2010 年汽车销售总量约 1800 万辆，气门挺柱需求量约 3 亿件以上。除气门挺柱外，活塞、活塞环、活塞销、柱塞、针阀、曲轴、凸轮轴、气门、链条和轴瓦等部位都需要 DLC 膜处理，市场需求量庞大，约 15 亿件[3]。开发具有自主知识产权的发动机配件低摩擦表面处理技术（超润滑 DLC 膜技术），推广该技术在中国汽车生产行业的应用，是解决国内汽车产业发展的瓶颈和提升行业竞争力的关键，也是解决汽车摩擦磨损问题的核心技术突破[4,5]。

1 现状与分析

国外很多汽车企业都已经开展了第 3 代表面处理技术（DLC 膜技术）的研究，如 Ford 公司将 DLC 膜应用于气门挺柱表面后，节约 1%的燃油[6]。日本 Nissan 公司的无氢 DLC 碳膜应用于气门挺柱后，可以将凸轮与气门挺柱间的摩擦减少约 40%。此外，Nissan 将该薄膜材料逐步投入到发动机的所有关键零部件上，预计节约燃油 2%[7]。

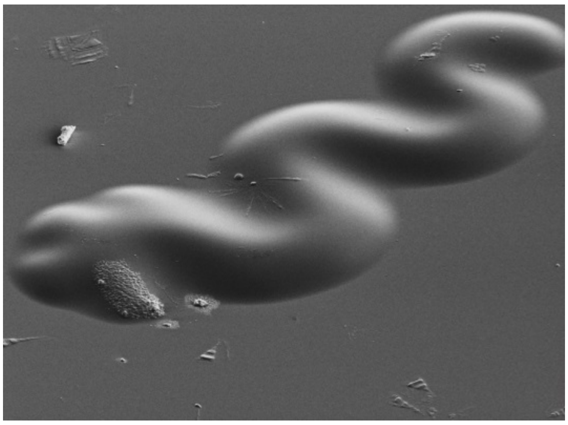
目前，国内发动机表面处理技术仍处在第 2 代技术水平，如涂敷 MoS_2、Au/Ag、石墨及渗碳、渗氮等表面处理技术。DLC 膜技术研究刚刚起步，对于 DLC 膜处理的工件只能依赖进口，这大大限制了 DLC 膜处理配件在国产发动机上的使用，也无形中降低了国内汽车产业在国际市场上的竞争力。

1.1 内应力起源

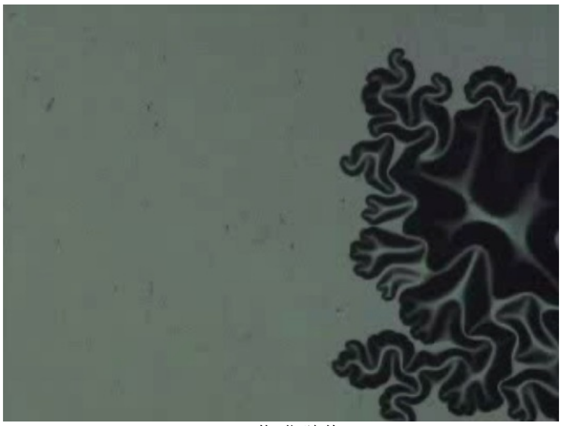
由于 DLC 膜具有高硬度、低摩擦系数、高耐磨性以及良好的化学稳定性等，因此其具有广阔的应用前景。DLC 膜制备技术的要领是如何降低薄膜内应力，从而改善膜/基结合力。DLC 膜较高内应力主要源于成膜过程中 sp^3 杂化键发生扭曲，造成复杂且高度交联碳网络变形程度提高，形成了内应力。有时内应力高达 10GPa，导致制备出的 DLC 膜鼓包\起皮并从基材脱落（参见图 1），从而失去实用价值。

薄膜内应力(σ)主要由 3 部分构成[8,9]：$\sigma=\sigma_T+\sigma_g+\sigma_m$，其中$\sigma_T$为薄膜从沉积温度向室温冷却过程中的温度变化。$\sigma_T=\text{CTE}\times\Delta T=\frac{E_f}{1-\nu_f}\int_{T_{dep}}^{T_{rm}}(\alpha_s(T)-\alpha_f(T))\mathrm{d}T$，其中 T_{dep}、T_{rm} 分别是沉积温度与室温，E_f、ν_f 分别是薄膜弹性模量和泊松比，$\alpha_f(T)$、$\alpha_s(T)$ 分别是薄膜和基材的热膨胀系数。由于薄膜与基材之间的热膨胀系数不同，从而在薄膜内部引起应力。

σ_g 为薄膜生长过程中由于荷能离子轰击导致碳-碳键长\键角变化，空间网络节点扭曲，从而在薄膜内部引起的应力，可以通过调节掺杂元素及荷能离子能量进行调控。荷能离子能量 U_k 与制备参数（如靶功率密度 D_w，基材偏压 V_s，气体压力 P_g）的关系为：



a　薄膜鼓包



b　薄膜脱落

图 1　自身内应力引起的 DLC 薄膜鼓包脱落（50×）
Fig. 1 DLC coatingsonsubstrate due to internal stress: a) blister, b) peeling off

$U_{\mathrm{k}} \propto \frac{D_{\mathrm{w}} V_{\mathrm{s}}}{P_g^{1/2}}$。$\sigma_{\mathrm{m}}$ 为金属掺杂 DLC 膜各组元材质力学性质不匹配引起的薄膜内应力，可以通过调节组元种类、数量及分布形态进行调控。

多层膜结构设计是降低硬质薄膜内应力的有效手段，不同研究者[10-12]采用磁控溅射技术，制备了纳米多层膜结构薄膜，探讨了不同调制周期下，薄膜力学性能的变化特点。结果表明，采用纳米多层膜结构，可以显著地降低薄膜的内应力。与之类似，发明专利（专利号 ZL201510099972. 5）[13]提出通过将 sp^3 键含量不同的软子层（sp^3 含量较低）、硬子层（sp^3 含量较高）交替叠加，获得具有多层膜结构特征的类金刚石膜，其中不涉及到引入外加异质层，有效避免了异质层引起薄膜力学性能恶化的难题，并且大大降低了层与层之间的内应力。本文关于多层膜结构不做过多涉及，重点论述异质元素掺杂降低类金刚石膜的内应力。

1.2　单元素掺杂

为了降低 DLC 膜的内应力，国内外科技工作者展开了掺杂元素对 DLC 膜内应力影响的研究[8,9,14-16]。掺杂异质元素能够改变 DLC 膜中 sp^3 和 sp^2 杂化键的比例，调整键角与键长畸变，促使非晶碳基质网络结构重整。通过控制掺杂元素与碳基质网络的成键方式、含量及存在状态，可有效缓解 DLC 膜内应力。通常，可供掺杂的异质元素分为两类：一类为碳化物形成元素，如 Si[17-24]、Ti[9, 25-31]、N[32-36]、Cr[37-40]、B[41,42]、Mo[43,44]、Zr[45,46]、W[47]、F[48]等；另一类为非碳化物形成元素，如 Cu[49-54]、Ag[55-58]、Al[9]、Ni[59]、Zn[60]、P[61]等。研究结果表明，除 Si 元素外的大部分掺杂元素，随着掺杂含量的增加，类金刚石膜内 $I_{\mathrm{d}}/I_{\mathrm{g}}$ 增加，sp^2 含量增多，sp^3 含量减少。赵等人[62]在前人研究的基础上指出掺杂 Si 能够有效降低薄膜内应力，但同时会降低薄膜硬度。他们认为 Si—C 键的能量（3. 21eV）小于 C—C 键的能量（3. 70eV），因此 Si 周围碳键的畸变得到松弛，内应力大幅下降，但键能的变小会使薄膜硬度降低。在碳化物形成元素掺杂 DLC 膜系中，掺杂金属元素 Ti 受到较多关注。Zhang 等[9,25]指出，Ti 含量较少时，Ti 原子处于非晶碳基质网络的间隙位置或以单质形态存在于非晶碳基质中，从而降低了非晶碳基质网络中由于键角扭曲而产生的残余应力。增加 Ti 含量，一部分 Ti 原子将与 C 原子键合生成硬质的 TiC 纳米晶，同时碳基质结构中 sp^3 杂化键减少。此时，掺杂 Ti 降低了薄膜内应力，但是薄膜硬度也有一定程度的下降。当继续增加 Ti 含量时，碳基薄膜中形成了越来越多的硬质 TiC 晶粒，大量弥散分布的 TiC 晶粒对碳基薄膜的强化作用增强，薄膜硬度不会下降。但此时薄膜摩擦系数增加，摩擦学性能恶化[63]。

与碳化物形成元素不同，非碳化物形成元素掺入 DLC 膜时，金属原子以非晶或者纳米晶金属团簇形态弥散分布于非晶碳基质中[9,49-60]。通常认为，非碳化物形成元素不与碳发生键合反应，但能占据一定的晶格位置，对薄膜释放内应力起促进作用。纳米晶金属团簇与非晶碳基质之间为非共格界面，易发生界面滑移，也能够对薄膜释放内应力起一定的促进作用[9,51]。Luo 等人[64]展开了掺杂金属元素铜对 DLC 膜性能影响的研究。结果表明：1）与银、铝等元素类似，金属元素铜不与碳元素发生化学反应生成碳化物（参见图 2）；2）掺杂的金属元素铜以纳米晶态存在于 DLC 膜非晶碳基质中（参见图 3）；3）掺杂不同含量的铜元素，显著改变 DLC 膜的 Raman 峰形（参见图 4）。非碳化物形成元素掺杂 DLC 膜能够有效地降低薄膜内应力，获得良好的摩擦学性能，但是过量掺杂往往会降低薄膜的机械强度。

1.3　二元或多元素掺杂

单一异质元素掺杂使得 DLC 膜实现某种优异性

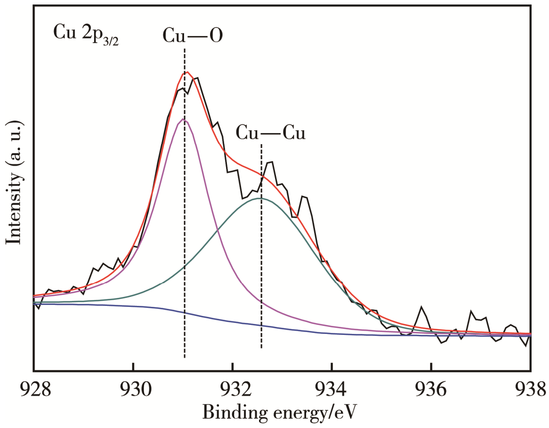


图 2　XPS Cu $2p_{3/2}$ 图谱（表明没有 C-Cu 化学键形成）[64]
Fig.2 XPS Cu $2p_{3/2}$ spectra (no C-Cu chemical bondforms)[64]

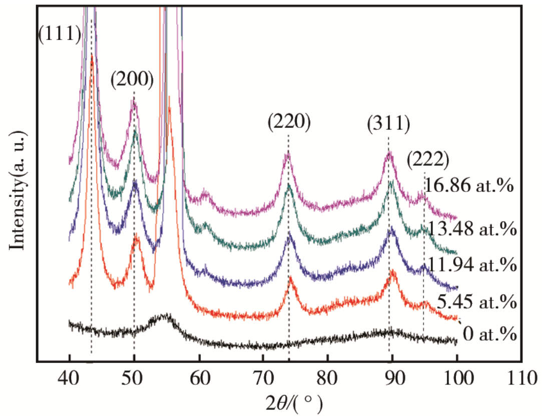


图 3　不同铜含量 DLC 膜的 XRD 图谱[64]
Fig.3 XRD spectra of DLC coatings with different Cu content[64]

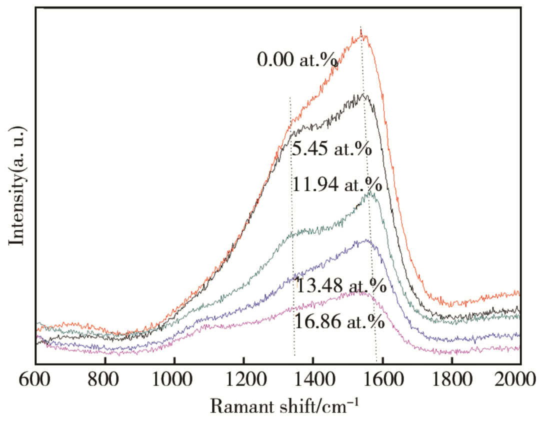


图 4　不同铜含量 DLC 膜的 Raman 图谱[64]
Fig.4 Raman spectra of DLC coatings with different Cu content[64]

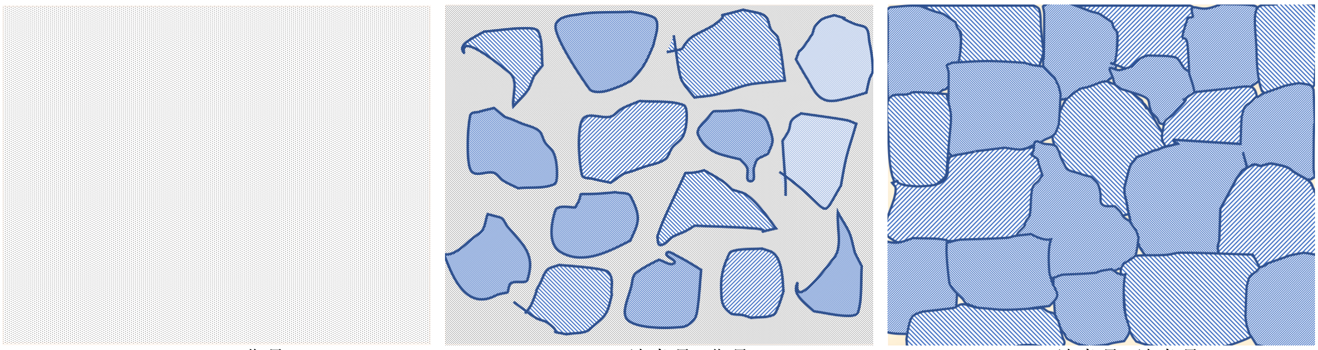
能的同时，也会导致其他性能的损失。通过对不同多元异质元素掺杂薄膜体系的研究，研究者们发现在碳基薄膜中同时引入两种或两种以上元素，可实现碳基薄膜内应力、硬度和摩擦学特性等综合性能的改善。目前研究比较多的是两种碳化物形成元素共掺杂类金刚石碳膜，研究对象通常有 Mo-W-C[65-69]、Si-N-C[70,71]、Ti-Si-C[72,73]、Ti-N-C[74]、Ti-Ta-C[75]、Ti-W-C[76]、Cr-N-C[77]、Si-F-C[78]、B-N-C[79]等体系。一种碳化物形成元素和一种非碳化物形成元素共掺杂类金刚石碳膜的研究实例相对较少，比如 Ti-Al-C[9,80]、Ti-Ag-C[81]、W-Al-C[82]、Ag-Si-C[83]、Cr-Al-C[84]、Cr-Cu-C[85]等体系，而两种非碳化物形成元素共掺杂类金刚石碳膜的研究实例更加鲜见报道。

两种碳化物形成元素共掺杂的类金刚石碳膜，其显微结构通常有 3 种类型：当掺杂元素含量较少或者沉积温度较低时，掺杂类金刚石碳膜表现为非晶形态（参见图 5a）；当掺杂元素含量较多或者沉积温度较高时，掺杂碳膜表现为由两种纳米晶构成的纳米复合结构（参见图 5c）；更多情况下，掺杂碳膜表现为一种纳米碳化物晶体周围包裹着非晶碳化物或者非晶碳（参见图 5b）。在二元异质碳化物形成元素掺杂类金刚石碳膜中，精确控制纳米晶碳化物形态、数量与分布是控制掺杂碳膜性能的关键。

在二元异质元素（一种碳化物形成元素和一种非碳化物形成元素）掺杂类金刚石碳膜中，精确控制纳米晶碳化物及纳米晶金属团簇数量、形态与分布是拟解决的关键科学问题。虽然掺杂碳化物形成元素能够缓解 DLC 膜内应力，调整薄膜硬度，但是过量掺杂金属元素会引起金属碳化物含量增加，恶化薄膜摩擦学性能。因此为了获得低应力、高硬度、良好摩擦学性能的薄膜，需要精确控制纳米晶碳化物数量、形态与分布。掺杂非碳化物形成元素能够缓解 DLC 膜内应力，调整薄膜摩擦学性能，但是，晶态金属团簇与非晶碳基质间易发生界面滑移，过量掺杂非碳化物形成元素会严重弱化 DLC 膜硬度。因而，需要精确控制纳米晶金属团簇数量、形态与分布。

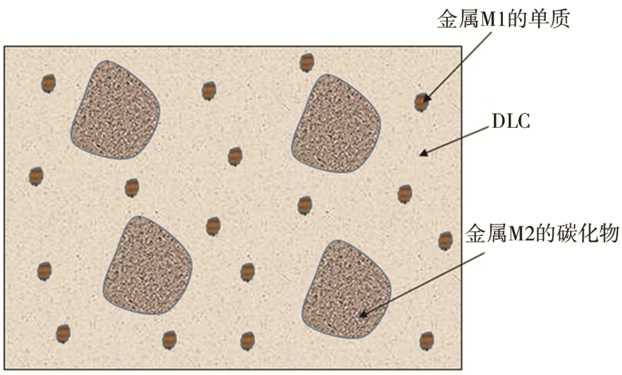
近年来，在二元异质元素掺杂的基础上，进一步发展出了多元异质元素共掺杂，如 Cr-Al-Si-C[86,87]、Ti-Al-Si-C[88]等体系，通过控制纳米晶尺度、形态与分布，形成复杂晶界等方式构建纳米复合结构，协同降低类金刚石碳膜内应力，期望获得优异的综合机械性能。

在上述分析的基础上，本课题组首次提出金属钛铜共掺杂类金刚石膜系（Ti-Cu-C 膜系），尝试将纳米复合结构引入 DLC 膜（参见图 6），通过二元金属掺杂协同作用降低 DLC 膜内应力，期望在降低 DLC 膜内应力的同时，获得优良的综合机械性能。相比于 Al，金属 Cu 是常见的金属固体润滑材料，摩擦过程中 Cu 向界面扩散能够改进润滑性；相比另一金属固体润滑材料 Ag，金属 Cu 成本较低，因此选择 Cu 作为非碳化物形成元素。通过精确控制掺杂金属元素 Cu 的含量，降低薄膜内应力的同时能够保持良好的摩擦学性能。选择常见金属元素 Ti 作为碳化物



a　非晶　　　　b　纳米晶+非晶　　　　c　纳米晶+纳米晶

图 5　两种碳化物形成元素共掺杂类金刚石碳膜的显微结构示意图
Fig.5 Schematic diagram ofDLC microstructure co-doped withtwo kinds of carbide forming elements: a) amorphous phase, b) nanocrystal+amorphous phase, c) nanocrystal+nanocrystal phases



注：M1—非碳化物形成元素，M2—碳化物形成元素

图 6　金属掺杂 DLC 膜显微结构示意图
Fig.6 Schematic diagram of metal-dopedDLC microstructure

形成元素，通过精确控制掺杂金属元素 Ti 的含量，控制碳化物纳米晶粒及其在非晶碳基质中的分布，降低薄膜内应力的同时能够保持较高的硬度，改善薄膜耐磨损性能。

2　研究方向与展望

元素掺杂降低类金刚石碳膜内应力的研究从最初的单一元素掺杂，逐步发展到二元或多元元素掺杂，从碳化物形成元素掺杂、非碳化物形成元素掺杂，逐步发展到碳化物形成元素与非碳化物形成元素的多元共掺杂，所研究的类金刚石碳膜的显微结构也从最初的非晶态结构向多元、多相结构发展，以期获得良好的综合机械性能。此外，计算机模拟技术在研究材料键长、键角等微结构等方面也发挥着越来越大的作用。在元素掺杂降低类金刚石碳膜内应力研究上，作者认为有以下方面需要注意：

1）单一元素掺杂类金刚石碳膜降低应力的研究，虽然目前做了大量的工作，但有些结果相互矛盾，需要进一步探讨掺杂元素对 DLC 膜中相互交联碳基质网络的成键方式、薄膜表面化学状态、sp^3 和 sp^2 杂化键的比例及活性悬键数量的影响，澄清其物理机制。

2）二元或多元元素掺杂类金刚石碳膜协同降低内应力的研究包括：待掺杂元素含量优化；掺杂元素在碳基质中成键状态；碳化物形成元素与碳形成的碳化物纳米晶，其形态与分布对 DLC 膜内应力、硬度、摩擦学性能的作用机理；非碳化物形成元素，其存在形态（非晶态或者纳米金属团簇）及分布对降低薄膜内应力的作用机理，其纳米金属团簇与非晶碳基质的非共格界面对薄膜内应力、硬度、摩擦学性能的作用机理。需要从杂化键等物理角度分析、研究多元素掺杂协同降低内应力机理。

3）在充分研究单元或多元元素掺杂类金刚石碳膜的基础上，探索开发同时适用不同应用环境（温度、适度、载荷）的自适应自修复类金刚石碳膜。

4）不同掺杂方式的综合运用及一些新的掺杂手段需要引起注意，比如高功率脉冲磁控溅射与离子源复合、磁控溅射与磁过滤阴极弧复合等。

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