基片偏压对MCECR溅射硬碳膜特性的影响

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摘 要 采用封闭式电子回旋共振(MCECR)氩等离子体溅射碳靶的方法在硅片上沉积了高质量的硬碳膜,膜层厚度约40 nm. 使用X射线光电子能谱仪(XPS)和高分辨率透射电子显微镜(HRTEM)分析了碳膜结构,并用POD摩擦磨损仪测试了碳膜的摩擦磨损特性,用纳米压入仪测试了碳膜的纳米硬度. 详细研究了基片偏压对碳膜的结构、摩擦磨损特性以及纳米硬度的影响,得到了最佳基片偏压.

关键词 MCECR溅射;硬碳膜;摩擦特性;纳米硬度;薄膜结构
中图分类号 O484.4 **文献标识码** A

0 引言

MCECR等离子体具有高的等离子体密度($10^{10}\sim10^{12}$ cm^{-3})、低的离子温度以及在低压(0.1到0.01 Pa之间)条件下放电等优点,在许多等离子体工艺中得到了广泛应用,如薄膜沉积以及刻蚀等. 厚度为1 nm到1 μm的硬碳膜在微电子、磁记录媒介以及机械保护等领域的应用越来越广泛[1-3]. 尽可能地增加sp^3的含量是制备该薄膜的主要研究方向. 文献[4]报导了非晶碳膜中sp3的含量已经超过80%. 根据常规的知识,这个想法是合情合理的,那就是sp^3的立方结构对碳膜硬度的贡献. 另一方面,近来,已经发现主要含有sp^2的碳膜的硬度已接近金刚石的硬度[5],其原因是,在碳膜中的sp^2纳米晶的作用是用来连接给薄膜贡献硬度的相邻的sp^3键[6].

本文采用MCECR氩等离子体溅射碳靶的方法在硅片上沉积了碳膜,测试了所沉积碳膜的各种性能,详细研究了基片偏压对碳膜结构、摩擦磨损特性以及纳米硬度等的影响.

1 实验方法

图1是MCECR等离子体溅射装置的结构示意图. 获得ECR等离子体的微波电源的频率为2.45 GHz,最大功率为500 W,被溅射的碳靶长度为46 mm,内径为110 mm,位于镜面场的中间. 采用直流电源溅射靶材,其变化范围可到1000 V. 基片不用水冷和加热,但采用等离子体沉积薄膜60 min后基片温度从室温上升到420 K. 基片可以是悬浮电位,也可以加 −120 V— +120 V的偏压. 镀制前真空室的本底真空度为2×10^{-4} Pa,充氩气后进行镀制时的真空度为2×10^{-2} Pa,碳膜被镀制在Si片上,厚度约为40 nm,用纳米压入仪测量薄膜的纳米硬度,采用H-9000高分辨率透射电子显微镜(HRTEM)测量薄膜的显微结构,其分辨率为0.19 nm,以及使用X射线光电子能谱仪测量碳膜中sp^2和sp^3的比例.

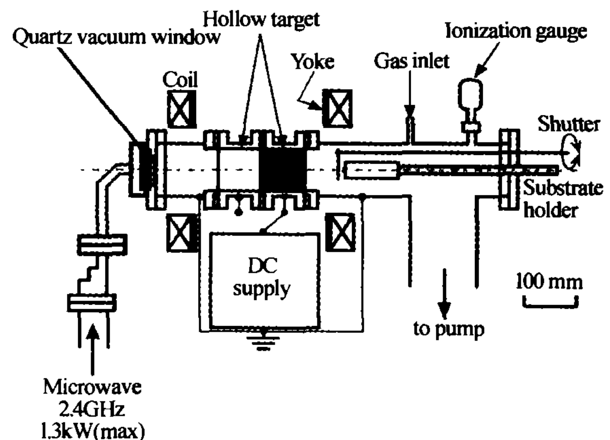

图1 MCECR等离子体溅射实验装置示意图
Fig. 1 Schematic diagram of MCECR plasma sputtering experimental apparatus

2 结果与讨论

2.1 薄膜的纳米结构

图2是基片偏压为 +30 V(a)和 +80 V(b)时镀制的薄膜的高分辨率透射电子显微镜(HRTEM)照片. 图3是两个样品中碳峰的XPS谱. Diaz等人报道了关于采用XPS分析碳峰中sp^2和sp^3含量的有效性[7]. 两个样品的光谱都由两个部分组成,即284.14 eV和284.73 eV,分别对应sp^2和sp^3. 图3中在285.38 eV的小峰是C-O键. XPS谱表明薄膜的键结构是由sp^2和sp^3组成的,而且sp^2是主要的. 在样品a,b中,sp^3/sp^2的比率分别为0.44和0.62.

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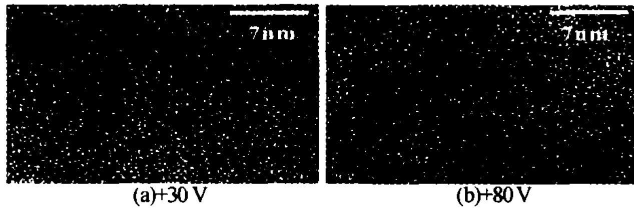

(a)+30 V　　(b)+80 V

图 2　MCECR 溅射碳膜的 HRTEM 照片

Fig. 2　HRTEM images of MCECR-sputtered carbon films

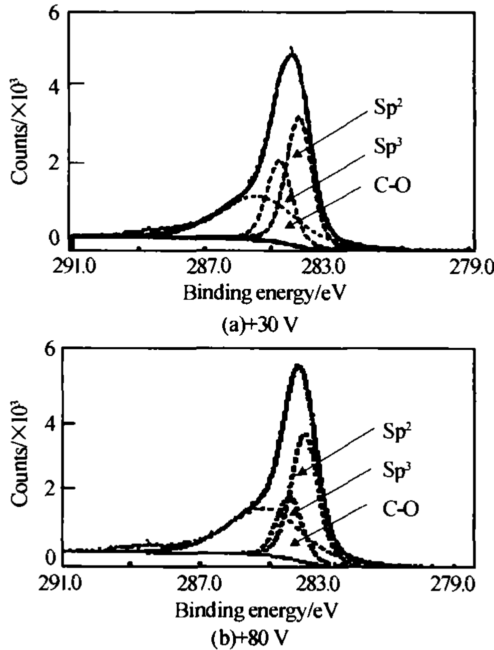

图 3　MCECR 溅射碳膜的 XPS 分析

Fig. 3　C1s XPS spectra of MCECR-sputtered carbon films

(a)+30 V　　(b)+80 V

图 4　MCECR 溅射的碳膜和硅片界面的 HRTEM 照片

Fig. 4　HRTEM images of the interface between the silicon substrate and the carbon film

图 4 表示了碳膜与硅片结合界面的 HRTEM 照片，可以很清楚地看到，样品 b 有破坏（黑区），而样品 a 没有. 可见，基片偏压对膜层的结构和成分有重要影响.

2.2　薄膜的机械性能

纳米压入仪测试硬度实验是用美国 Hysitron Inc. 公司的纳米压入仪进行的. 典型的加载和卸载曲线见图5. 薄膜硬度随基片偏压的变化曲线见图6.

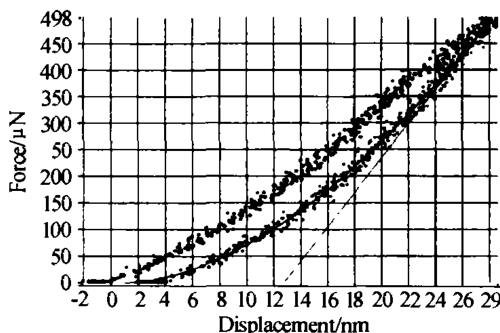

图 5　采用纳米压入仪测量的加载和卸载典型曲线

Fig. 5　Typical indentation load-displacement curve of sample

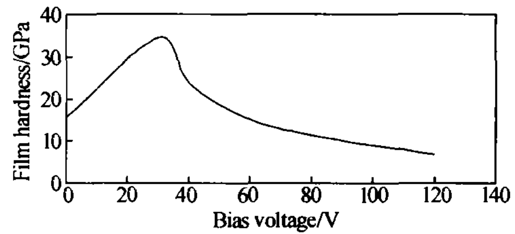

图 6　膜层硬度和基片偏压之间的关系

Fig. 6　Relationship between film hardness and bias voltage

从图中可以很清楚地看出，薄膜硬度依赖于基片的偏压，在基片偏压为 +30 V 时，薄膜的硬度值最大，约 34 GPa.

2.3　薄膜的摩擦特性

摩擦测试采用 POD 摩擦磨损仪，摩擦球为半径为 2 mm 的 SiC 球. 实验之前采用在酒精中超声波清洗SiC球和被测的碳膜. 负载调整范围是 1 N ~ 10 N. 图 7(a) 是负载为 1N，滑动速度为 50mm/s，薄膜是在基片偏压为 +30 V 时镀制的，采用 SiC 球进行实验得到的摩擦系数曲线. 从图中可见，在 3900 圈以前，摩擦系数保持在一个非常稳定的值 0.11，但到了 3900 圈时，摩擦系数突然上升. 3900 圈以后，摩擦系数上升为 0.4，这主要是由于膜层破坏引起的. 在基片偏压为 +80V时，薄膜的摩擦系数为0.15，

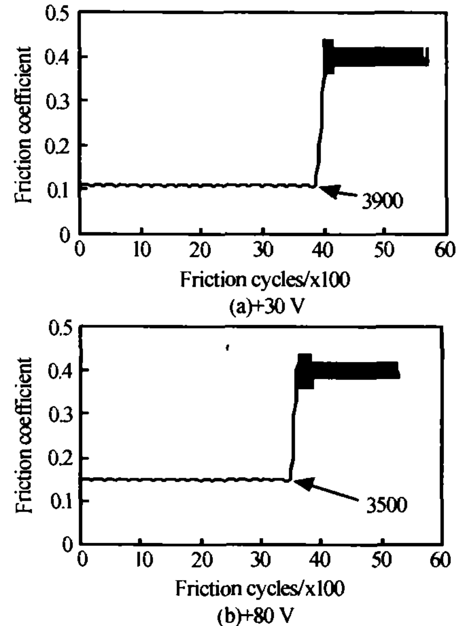

图 7　膜层的摩擦系数和寿命

Fig. 7　Friction coefficient and lifetime of carbon films

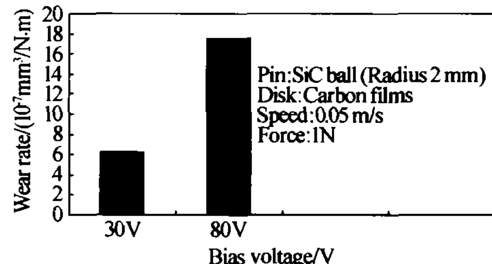

图 8　偏压为 +30 V 和 +80 V 时膜层磨损率的比较

Fig. 8　Comparison of wear rate between +30 V and +80 V biases

磨损寿命为3500圈,如图7(b).可见基片偏压对薄膜的摩擦特性是有影响的.另一方面,采用POD摩擦磨损仪和轮廓仪测试了薄膜的磨损率,图8表示了在偏压为+30 V和+80 V时他们磨损率的比较,从中可以看出,偏压为+80 V的磨损率明显比偏压为+30 V的磨损率高.

3 结论

本文采用MCECR等离子体溅射的方法在硅片上沉积了高质量的硬碳膜,膜层厚度约40 nm.研究了基片偏压对采用此方法制备的硬碳膜的特性的影响,获得了较好的基片偏压(+30V).XPS和HRTEM分析表明膜层的键结构主要是sp^2,采用纳米压入仪测试出的薄膜的最大硬度约为34 GPa,采用POD摩擦磨损仪所测量的薄膜的摩擦系数约为0.1~0.15,磨损率为6.23×10^{-7} mm^3/Nm~1.75×10^{-6} mm^3/Nm.研究结果表明,基片偏压对硬碳膜的特性有重要影响.

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Influence of Substrate Bias on the Properties of Hard Carbon Films Prepared by MCECR Sputtering

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Abstract The carbon films exhibit a variety of useful properties such as a hardness approaching that of a diamond, transparency, a smooth surface morphology, wear resistance and chemical inertness, and were widely applied in the fields of mechanics, electronics, optics, and magnetic, and so on. Experimental studies to obtain high quality hard carbon films were conducted using a Mirror-Confinement-type Electron Cyclotron Resonance (MCECR) plasma sputtering method. The carbon films with 40 nm thickness were deposited on Si by sputtering the carbon target with Ar^+. The structure of carbon films was analyzed using the X-ray photoelectron spectropscopy (XPS) and high-resolution transmission electron microscopy (HRTEM), the tribological properties were measured using the Pin-on-Disk tribometer, and the nanohardness was measured using the nanoindenter. The effect of substrate bias on the structure, tribological properties, and nanohardness of carbon film was studied in detail, and the best substrate bias was obtained.

Keywords MCECR sputtering; Hard carbon films; Friction characteristics; Nanohardnes; Film structure

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