螺旋波等离子体合成 SiON 薄膜及其特性

於俊^{1,2}, 黄天源^{1,2}, 季佩宇^{1,2}, 金成刚^{1,2}, 诸葛兰剑^{1,3}, 吴雪梅^{1,2*}

1. 苏州大学物理与光电能源学部, 苏州纳米科技协同创新中心, 苏州 215006;

2. 江苏省薄膜材料重点实验室, 苏州 215006;

3. 苏州大学分析测试中心, 苏州 215123

* 联系人, E-mail: xmwu@suda.edu.cn

2016-10-23 收稿, 2016-11-22 修回, 2016-11-24 接受, 2017-01-10 网络版发表

国家磁约束聚变项目(2014GB106005, 2010GB106000)和国家自然科学基金(11175126, 11375126, 11435009, 11505123)资助

摘要 采用不同比例的 N_2/Ar 螺旋波等离子体(HWP), 对Si表面进行氮化处理合成SiON薄膜. X射线光电子能谱(X-ray photoelectron spectroscopy, XPS)结果显示, SiON薄膜主要由Si-O-N和Si-N键的两相结构组成. 原子力显微镜结果表明氮化层光滑平整, 薄膜表面粗糙度小于1.2 nm. 水接触角的测量表明经过等离子体处理后样品表面疏水性能提高. 放电过程中通过发射光谱采集了不同 N_2 和Ar流量比放电时的光谱数据, 研究了等离子体中的粒子与SiON薄膜结构之间的关系.

关键词 螺旋波等离子体, SiON, 发射光谱, X射线光电子能谱, 原子力显微镜

SiON因其高硬度、耐腐蚀、耐高温、抗氧化等许多优良的力学及化学性质使其成为新一代的功能薄膜材料^[1]. 据报道, SiON涂层在光学器件方面有着重要的应用, 其可作为高精度光学透镜、移动电话的触控屏、平板电脑的触控板、波导管等器件的保护层. SiON涂层的莫氏硬度高达9 H, 在可见光范围内, 其透过率高达98%^[2].

除此之外, SiON在微电子领域也有着重要的应用. 据报道, 对于热载流子的注入、杂质扩散和水汽渗透^[3~5], SiON有着非常好的抑制作用. SiON作为介电层, 具有较高的电子迁移率和电子陷阱能级密度^[6], 目前主要通过等离子体增强化学气相沉积(PECVD)的方法制得. 用于PECVD的等离子体源主要包括感性耦合等离子体源(ICP)、容性耦合等离子体源(CCP)和微波电子回旋共振等离子体源(ECR). 随着对PECVD研究的深入, 人们发现PECVD的反应选择性较差, SiON介电层不可避免地存在着杂质, 例

如: H的存在, 将会影响其绝缘性和介电性^[7], 这制约了SiON在大规模集成电路中的应用.

螺旋波等离子体源(HWP)因其在较低的气压(0.1~10 Pa)下能够激发高密度(约为 10^{13} cm^{-3})等离子体而被人们广泛关注^[8,9]. 高能电子与反应气体粒子持续地碰撞激发, 有效地维持了螺旋波的放电过程. 本实验中, 稳定的螺旋波混合气体放电, 能够得到高离解率的 N_2 等离子体, 有利于合成高质量SiON薄膜.

1 实验方法

本实验装置, 由水冷磁场线圈、Nagoya III 右旋型天线、放电腔室、基片台、发射光谱、EQP质量能量分析仪组成. 装置本底真空为 $1 \times 10^{-4} \text{ Pa}$, 射频源频率为13.56 MHz, 详细参数可参考本课题组已发表的文献^[10]. 实验时, 首先将基片 $1 \text{ cm} \times 1 \text{ cm}$ p-Si(100)片经丙酮、酒精和去离子水超声清洗, 然后将基片固定在基片台上. 最后将Ar(99.999%)和 N_2 (99.999%)按一定

引用格式: 於俊, 黄天源, 季佩宇, 等. 螺旋波等离子体合成 SiON 薄膜及其特性研究. 科学通报, 2017, 62: 2125~2131

Yu J, Huang T Y, Ji P Y, et al. Synthesis of SiON films by helicon-wave plasma and their characteristic analysis (in Chinese). Chin Sci Bull, 2017, 62: 2125~2131, doi: 10.1360/N972016-01182

的比例通入放电腔室内放电, 比例如表1所示. 放电功率为1500 W, 外加磁场为1100 Gs ($1 \text{ Gs}=1 \times 10^{-4} \text{ T}$), 等离子体处理时间10 min, 放电气压为0.1~0.5 Pa.

等离子体放电图片采用佳能EOS7DMark II 相机拍照, 光谱诊断采用的是荷兰Avantes公司生产的AvaSpec-2048FT-8-RM型光纤光谱仪. 薄膜的表面粗糙度采用Bruker公司的原子力显微镜(AFM)表征, 用Thermo Fish公司生产的ESCALAB 250Xi型XPS表征薄膜的表面成分. 所得图谱用C-C键的结合能284.8 eV校正. SL200A型接触角测量仪测定微滴与薄膜间的接触角.

2 实验结果与讨论

在 N_2/Ar 比例较低时, 放电气体颜色为蓝色, 随着 N_2 含量的增多, 颜色逐渐向暗红色转变, 如图1所示, 表明随着 N_2 含量的增加, 放电模式逐渐从螺旋波向ICP模式转变^[11].

图2为 N_2 含量为50%的螺旋波放电时的发射光谱图. 图中 N_2 的峰位隶属于 N_2 第一正带系(FPS)和第二正带系(SPS), 而 N_2^+ 的峰位则隶属于 N_2^+ 第一负带系(FNS)^[12]. Ar的峰位主要集中在400~500 nm之间. 从发射光谱图, 得到 N_2^+ (391.4 nm)和Ar (480.6 nm)的基团谱线强度随 N_2 流量变化的关系图. 如图3所示, 从图上可以发现, N_2^+ 的浓度随着 N_2 含量增加而增加, 当 N_2 流量的百分比为50%时, N_2^+ 的浓度达到最大值. 这是因为随着 N_2 含量的增加, 促使 N_2^+ 的浓度增大, 当 N_2 含量超过50%时, 混合气体放电模式由螺旋波模式转变为ICP模式, 从而导致 N_2^+ 的浓度降低. 在相同

的气压和射频功率条件下, N_2 基团的谱线强度正比于 SiON 薄膜沉积的相应前驱体的浓度^[13]. 因此, 选择 N_2 含量为50%的螺旋波等离子体对基片表面进行氮化处理, 处理时间为10 min, 通过XPS对等离子体处理后的Si表面进行深度剖析, Ar离子剖析速率为0.05 nm/s, 如图4和5所示.

图4(a)~(d)分别是剖析时间为0, 100, 200和300 s时的N 1s深度剖析图谱. 在剖析前(图4(a)), N 1s的光电子峰位可以很好地拟合为Gaussian单峰, 结合能为399.3 eV, 属于 SiON , 由于硅表面通常都有自然氧化层 SiO_2 的存在, 因此, 经氮化处理后Si的外表面以 SiON 存在. 当剖析时间为100 s时(图4(b)), N 1s的光电子峰位可以拟合为Gaussian双峰, 结合能分别为399.3和398.4 eV, 分别对应 SiON 和 Si_3N_4 ^[4]. SiON 和 Si_3N_4 所占的百分比分别为73%和27%; 剖析时间为200 s时, SiON 的百分比下降为24%, 而 Si_3N_4 所占的百分比上升为76%, 剖析时间增加到300 s(图4(d))时, N 1s的光电子峰位几乎不可见. XPS的深度剖析结果表明, 超薄氮化层的内层以 Si_3N_4 为主, 外层以 SiON 为主; 根据剖析速率为0.05 nm/s, 表明超薄氮化层厚度为15 nm左右.

表1 螺旋波放电时Ar和 N_2 的流量

Table 1 The flow rate of N_2/Ar helicon-wave discharge

参量	a	b	c	d	e	f	g
Ar(sccm)	17.5	15	12.5	10	7.5	5	2.5
N_2 (sccm)	2.5	5	7.5	10	12.5	15	17.5
$\text{N}_2/(\text{N}_2+\text{Ar})(\%)$	12.5	25	37.5	50	62.5	75	87.5

图1 (网络版彩色)不同 $\text{N}_2/\text{N}_2+\text{Ar}$ 流量比的混合气体放电图. (a) 12.5%; (b) 25%; (c) 37.5%; (d) 50%; (e) 62.5%; (f) 75%; (g) 87.5%

Figure 1 (Color online) The pictures of different flow-rate ratio of $\text{N}_2/\text{N}_2+\text{Ar}$. (a) 12.5%; (b) 25%; (c) 37.5%; (d) 50%; (e) 62.5%; (f) 75%; (g) 87.5%

图2 (网络版彩色) N_2 含量为 50% 时 N_2 /Ar 混合气体放电发射光谱图

Figure 2 (Color online) Optical emission spectra of N_2 /Ar plasma. Discharge conditions: 50% N_2

图3 (网络版彩色) N_2^+ (391.4 nm) 和 Ar (480.6 nm) 谱线的强度随 N_2 含量的变化关系图

Figure 3 (Color online) The intensity of N_2^+ (391.4 nm) and Ar (480.6 nm) as a function of the N_2 concentration

从 Si 2p 的深度剖析图谱也可得到相同的结果, 如图5(a)~(d)所示. 当刻蚀时间为 0 s (图5(a)), Si 2p 的光电子峰位结合能为 102.5 eV, 表明经氮化处理后表面为 SiON. 当剖析时间为 100 s (图5(b)), Si 2p 的光电子峰可分峰为 101.4 eV 的 Si_3N_4 和 102.5 eV 的 SiON. 剖析时间为 200 s 时 (图5(c)), 结合能为 101.4 eV 的 Si_3N_4 峰增强, 而 102.5 eV 的 SiON 峰减弱; 同时出现 Si

2p 结合能为 99.3 eV 的 Si 峰. 当刻蚀时间为 300 s 时 (图5(d)), 只有基底的 Si 峰存在. 通过以上分析, Si 表面经螺旋波放电氮化处理, 外层主要以 SiON 的形式存在, 而贴近硅表面的内层主要以 Si_3N_4 的形式存在. 而 O 应来自 Si 表面自然氧化层 SiO_2 中的 O, 如图6所示的空白硅片 XPS 深度剖析的 O 1s 结合能强度的变化, 空白硅片氧化层约 10~15 nm.

Si 表面经氮化处理后, 表面仍非常平整, 随着 N_2 含量的增多, 表面越来越平整, 见图7(a)~(d) 的 AFM 三维图; 且均方根粗糙度 RMS 从 N_2 含量 12.5% 的 1.2 nm 减少到 N_2 含量 75% 的 0.4 nm, 如图7(e) 所示, 这说明, 所沉积的 SiON 薄膜较为平整、均匀.

图8是4组样品测水接触角时水滴的形态图. 接触角是指在气、液、固三相交点处所作的气-液界面的切线经过液体内部与固-液交界线之间的夹角 θ , 可以很方便地用于评价样品的亲水性程度. 若 $\theta < 90^\circ$, 则固体是亲水性的, 润湿性好; 反之, 则固体是疏水性的, 润湿性较差. 图中经过等离子体处理过的样品的水接触角大于 Si 的水接触角, N_2 含量 50% 的样品的水接触角是所有样品中最大的, 这说明在螺旋波等离子体处理后, Si 表面由于氮化作用, 其疏水性能得到提高.

图4 (网络版彩色) N₂ 含量为 50% 时 XPS 图谱 N 1s 的深度剖析图. (a) 1 s; (b) 100 s; (c) 200 s; (d) 300 s

Figure 4 (Color online) Depth profiles of N 1s at the flow-rate of N₂ of 50%. (a) 1 s; (b) 100 s; (c) 200 s; (d) 300 s

图5 (网络版彩色) N₂ 含量为 50% 时 XPS 图谱 Si 2p 的深度剖析图. (a) 1 s; (b) 100 s; (c) 200 s; (d) 300 s

Figure 5 (Color online) Depth profiles of Si 2p at the flow-rate of N₂ of 50%. (a) 1 s; (b) 100 s; (c) 200 s; (d) 300 s

图6 (网络版彩色)空白Si片XPS图谱O 1s的深度剖析图
Figure 6 (Color online) Depth profiles of O 1s of Si

3 结论

本文采用 N_2/Ar 螺旋波等离子体,对Si表面进行氮化处理,在室温下,得到内层以 Si_3N_4 为主,外层以SiON为主的超薄氮化层,氮化层光滑平整,RMS小于1.2 nm,氮化层厚度约15 nm,样品表面疏水性能

图7 (网络版彩色)(a)~(d)不同 N_2 含量下的SiON的AFM三维图. (a) 12.5%; (b) 37.5%; (c) 50%; (d) 75%; (e) 均方根粗糙度RMS随 N_2 含量的变化图

Figure 7 (Color online) Diagrams of AFM at different flow-rate ratio of N_2 . (a) 12.5%; (b) 37.5%; (c) 50%; (d) 75%; (e) RMS roughness of the SiON film as a function of N_2 concentration

提高. 相比于其他CVD方法,螺旋波混合气体放电具有高密度、高离化率的特点,获得较高的 N_2 离解率,是一种新型的等离子体氮化方法,有利于高质量SiON薄膜的生长.

图8 水滴在不同样品上的形成状态. (a) Si; (b) 12.5%; (c) 37.5%; (d) 50%; (e) 75%

Figure 8 The formation of water droplets on substrate for different samples. (a) Si; (b) 12.5%; (c) 37.5%; (d) 50%; (e) 75%

参考文献

- 1 Zhang X, Ptasińska S. Growth of silicon oxynitride films by atmospheric pressure plasma jet. *J Phys D-Appl Phys*, 2014, 47: 438–446
- 2 Zhang Z B, Shao Z H, Luo Y M, et al. Hydrophobic, transparent and hard silicon oxynitride coating from perhydropolysilazane. *Polym Int*, 2015, 64: 971–978
- 3 Oka F, Tachikawa M, Tsukuda T, et al. Effects of postannealing of electrical characteristics and fowler-nordheim current stress resistance of Si oxynitride grown in helicon-wave-excited O_2 - N_2 -Ar plasma. *Jpn J Appl Phys*, 2000, 39: 1013–1021
- 4 Uchiyama A, Fukuda H, Hayashi T, et al. High performance dual-gate sub-halfmicron CMOSFETs with 6 nm-thick nitride SiO_2 films in an N_2O ambient. In: *Proceedings of Electron Devices Meeting. IEEE*, 1990. 425–428
- 5 Hwang H, Ting W, Kwong D L, et al. Electrical and reliability characteristics of ultrathin oxynitride gate dielectric prepared by rapid thermal processing in N_2O . In: *Proceedings of Electron Devices Meeting. IEEE*, 1990. 421–424
- 6 O'Meara D L, Wajda C, Dip A, et al. Method of forming uniform ultra-thin oxynitride layers. US Patent, US7202186, 2007-4-10
- 7 Kimura S, Ito T, Tabakomori M, et al. Si oxynitridation with helicon-wave excited nitrogen plasma: Effects of plasma divergence and concentration on substrates. *Jpn J Appl Phys*, 1997, 36: 316–319
- 8 Chen F F. Helicon discharges and sources: A review. *Plasma Sources Sci Tech*, 2015, 24: 014001
- 9 Yao Z Q, Harrison H B, Dimitrijević S, et al. Effects of nitric oxide annealing of thermally grown silicon dioxide characteristics. *IEEE Electron Device Lett*, 1995, 16: 345–347
- 10 Huang T Y, Jin C G, Yu J, et al. High magnetic field helicon plasma discharge for plasma-wall interaction studies. *Sci China-Phys Mech Astron*, 2016, 59: 645201
- 11 Celik M. Spectral measurements of inductively coupled and helicon discharge modes of a laboratory argon plasma source. *Spectrochim Acta-Part B*, 2011, 66: 149–155
- 12 Song M A, Lee Y W, Chung T H. Characterization of an inductively coupled nitrogen-argon plasma by Langmuir probe combined with optical emission spectroscopy. *Phys Plasmas*, 2011, 18: 557–583
- 13 Lu T, Xin Y, Wu X M. Study on a-SiN_x: H films prepared by ECR-CVD (in Chinese). *J Funct Mater Device*, 2006, 12: 259–263 [鲁涛, 辛煜, 吴雪梅. ECR-CVD 方法生长 a-SiN_x: H 薄膜的研究. *功能材料与器件学报*, 2006, 12: 259–263]

Summary for “螺旋波等离子体合成 SiON 薄膜及其特性”

Synthesis of SiON films by helicon-wave plasma and their characteristic analysis

YU Jun^{1,2}, HUANG TianYuan^{1,2}, JI PeiYu^{1,2}, JIN ChengGang^{1,2}, ZHUGE LanJian^{1,3} & WU XueMei^{1,2*}

¹ College of Physics, Optoelectronics and Energy, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215006, China;

² Key Laboratory of Thin Film Materials of Jiangsu Province, Suzhou 215006, China;

³ Analysis and Testing Center, Soochow University, Suzhou 215123, China

* Corresponding author, E-mail: xmwu@suda.edu.cn

SiON becomes a kind of new functional material because it has many excellent mechanical and chemical properties such as high hardness, corrosion resistance, oxidization resistance. It is reported that the coating of SiON has many important applications in optical device. For example, it can be used as the protective layer of Edmund optics, touch panel of mobile phone, waveguide tube et al. the Mohs hardness of SiON is about 9H. In addition, the transmittance of the coating is 98% in the visible region. Lately, lots of researchers are interested in the biomedical applications of SiON coatings due to its favourable mechanical properties and the good hemocompatibility of the material. Such as hip implants, it can help patient recover soon because the coating is smooth and the Si–N and Si–O–N chemical bonding are more to the hydrophilicity than Si–O or Si–Si bonds. There is also lots of significant application of SiON films in the field of microelectronics. According to the reports, SiON has the inhibiting effect on hot-carrier injection, impurity diffusion and water vapor permeability. As the dielectric layer, SiON also possesses better electronic mobility and the trap densities of electron. So far, the main synthetic method of SiON is plasma enhanced chemical vapor deposition (PECVD) including inductive coupled plasma source (ICP), capacitive coupled plasma source (CCP) and microwave electron cyclotron resonance (ECR). It is found that selectivity of PECVD is bad along with the further study of it. In addition, the SiON dielectric layer contains impurities unavoidably, for example, it will affect the insulation and dielectric properties if adding H atom into the dielectric layer, which can restrict application in large scale integrated circuit. Helicon wave plasma source (HWP) comes to the notice of many researchers because of its high density (about 10^{13} cm^{-3}) at low pressure (0.1~10 Pa). Chen said that “Interest in helicon discharges stems from their unusually high ionization efficiency: plasma densities n achieved are almost an order of magnitude higher than in other discharges at comparable pressures and input powers.” During the discharge, high-energy electron collides with gas particle adequately. In this experiment, it can divide N_2 into N_2^+ efficiently along with steady-state helicon wave discharge. In addition, there is no impurity element mixed in the SiON (such as C, H) which can improve the quality of the SiON films. In this experiment, SiON films were synthesized by nitridation on the surface of Si sputtered by N_2/Ar helicon-wave plasma. During the mixed helicon-wave discharge, the mass flow ratio of N_2 and Ar was different. X-ray photoelectron spectroscopy (XPS) showed that the SiON films were constituted of Si–O–N and Si–N. Atom force microscopy (AFM) indicated that the surface of the film was very flat and smooth, and the RMS was less than 1.2 nm. We collected Plasma discharge parameters by optical emission spectroscopy (OES) when the Si wafer was sputtered using N_2/Ar helicon-wave plasma, and studied the relationship between the particle in the plasma and structure of SiON films.

helicon wave plasma, SiON, optical emission spectrum, X-ray photoelectron spectroscopy, atomic force microscope

doi: 10.1360/N972016-01182