第 47 卷第 6 期　　红外与激光工程　　2018 年 6 月
Vol.47 No.6　　Infrared and Laser Engineering　　Jun.2018

Influence of thermal annealing on mechanical and thermoelastic characteristics of SiO_2 films produced by DIBS

Leng Jian, Ji Yiqin, Liu Huasong, Zhuang Kewen, Liu Dandan

(Tianjin Key Laboratory of Optical Thin Films, Tianjin Jinhang Institute of Technical Physics, Tianjin 300300, China)

Abstract: Mechanical and thermoelastic charecteristics of optical films are important to ensure the performance of optical coating systems. SiO_2 films were prepared by dual ion beam sputtering (DIBS) on Si <110> and Schott Q1. The mechanical and thermoelastic properties of films as-deposited and annealed were systematically investigated. The results show that reduced Young′s modulus (E_r) is elevated to 72 GPa while the film was annealed at 750 ℃, and hardness (H) increases to over 10 GPa. The as-deposited films show compressive stress and the stress could be dramatically released while annealed over 450 ℃, incicating that heat treatment could improve the internal stress of SiO_2 film. Poisson′s ratio (v_f) of annealed SiO_2 films is around 0.18, and Young′s modulus (E_f) of as-deposited and annealed films is larger than that of fused silica, and elevated over 50 GPa while annealed at 750 ℃. Thermal expansion coefficient (α_f) decreases from 6.78×10^{-7} ℃$^{-1}$ to the minimum value 5.22×10^{-7} ℃$^{-1}$ while annealed at 550 ℃.

Key words: dual ion beam sputtering (DIBS); SiO_2 film; annealing;
mechanical and thermoelastic characteristics

CLC number: O436　　**Document code:** A　　**DOI**: 10.3788/IRLA201847.0621002

热处理对双离子束溅射 SiO_2 薄膜力学及热力学特性的影响

冷　健，季一勤，刘华松，庄克文，刘丹丹

(天津市薄膜光学重点实验室 天津津航技术物理研究所，天津 300300)

摘　要：光学薄膜的力学及热力学特性决定了光学系统性能的优劣。采用双离子束溅射的方法在硅<110>和肖特石英 Q1 基底上制备了 SiO_2 薄膜，并对制备的膜层进行退火处理。系统研究了热处理前后 SiO_2 薄膜的力学及热力学特性。研究结果表明，750 ℃退火条件下 SiO_2 薄膜的弹性模量(E_r)增加到 72 GPa，膜层硬度增加到 10 GPa。镀完后未经退火处理的 SiO_2 薄膜表现为压应力，但是应力值在退火温度达到 450 ℃以上时急剧降低，说明热处理有助于改善 SiO_2 薄膜内应力。经退火处理的 SiO_2 薄膜泊松比(v_f)为 0.18 左右。退火前后 SiO_2 薄膜的杨氏模量(E_f)都要比石英块体材料大，并且 750 ℃退火膜层杨氏模量增加了 50 GPa 以上。550 ℃退火的 SiO_2 薄膜热膨胀系数(α_f)从 6.78×10^{-7} ℃$^{-1}$ 降到最小值 5.22×10^{-7} ℃$^{-1}$。

关键词：双离子束溅射； SiO_2 薄膜； 退火； 力学及热力学特性

收稿日期：2018-01-05；　**修订日期：**2018-02-11

基金项目：国家自然科学基金(61775167，61405145，61235011，61705165)；天津市自然科学重点基金(15JCZDJC31900)；
中国博士后科学基金(2015T80115，2014M560104)

作者简介：冷健(1983-)，男，高级工程师，博士，主要从事光学薄膜的制备及其特性方面的研究。Email:lenjianbit@aliyun.com

0 Introduction

SiO_2 films have the advantages of low refractive index, good stability and high mechanical strength. With the development of optical film, the research of SiO_2 films has been continuous and deepening. They have a wide range of applications from ordinary optical components to high-precision optical components[1-2], and they are also widely used in the semiconductor, chemical catalysis, biomedical, surface modification and pharmaceutical packaging.

SiO_2 films are traditionally produced by physical vapor deposition[3], and also by sol-gel[4] or chemical vapor deposition in specific fields. RF ion beam sputtering, due to the ion source technology, has the advantages of low pollution, high stability[5-6]. So it has been widely used in the production of high quality film, and it′s the only applicable technology in laser gyro mirror and other high quality requirements. Materials evaporated in RF sputtering as single molecules (atoms) or oligomeric molecules (atoms) could carry high energy (3-5 eV) by this method, so it′s able to obtain almost no macroscopic scale defects, high packing density, drift-free films. The properties of SiO_2 films prepared by ion beam sputtering were focused in this paper.

At present, the research of SiO_2 films is mainly focused on the refractive index, absorption characteristics, structural characteristics, spectral characteristics and so on[7-8]. There are few studies on the mechanical and thermodynamic properties of SiO_2 films, which is very important for optical components, determining films service life and environmental stability. So it is necessary to carry out relevant research. In this paper, the mechanical properties of SiO_2 films are obtained by continuous stiffness method. The thermoelastic properties are studied by double-substrate method on silica and Si<110>. The relationship between the annealing temperature and the mechanical properties such as the elastic modulus and the hardness of the SiO_2 film and the influence on the thermodynamic parameters of the SiO_2 thin film were determined. Which has a positive reference value for SiO_2 film preparation process.

1 Experiment

1.1 Film deposition and annealing

SiO_2 films were deposited on Φ25 mm×1 mm UV fused silica (Schott Q1) and Si<110> substrates, using the Spector DIBS system made by Veeco-Ion Technology. The system was equipped with two Kaufman ion sources, wherein the primary is 16 cm in diameter, and the secondary is 12 cm. SiO_2 target was $\Phi 14'' \times 0.5''$, with the purity of 99.995%. The substrates holder was rotated at 650 rpm during the sputtering process to ensure film uniformity. 25 sccm (standard-state cubic centimeter per minute) oxygen was discharged before target to get standard stoichiometric SiO_2 film. Argon flow for primary and secondary ion source was 16 sccm and 8 sccm, respectively. The deposition parameters are listed in Tab.1.

Tab.1 Fundamental fabrication conditions of SiO_2 films

Item	Value
Primary ion source voltage/V	1 250
Primary beam current/mA	600
Secondary ion source voltage/V	350
Secondary beam current/mA	90
Base pressure/torr (1 torr ≈ 133.322 Pa)	4×10^{-6}
Oxygen flow/sccm	25
Sputtering time/s	3 500

The key parameters in annealing process are annealing temperature (T_a) and design of annealing curve, and the process should not significantly change substrate material properties. Through ellipsometry analysis it was seen that after 750 ℃ annealing, Si<110> substrate had weak oxidation at the substrate-film interface. So the annealing temperature was chosen from 150 ℃ to 750 ℃ (far less than the melting point of quartz material), 100 ℃ for the interval.

The annealing curve is divided into three regions: heating zone, soaking zone and cooling zone. The heating rate k was chosen as 2 ℃/min and the soaking temperature was kept constant for 24 h to ensure SiO_2 films finishing modification. After annealing, samples were cooled down naturally.

1.2 Mechanical characterization

The mechanical properties of SiO_2 films were described by nanoindentation measurement (Nano Indenter G200, Agilent Tech.), and Berkovich indenter was chosen during the measurement. The load and displacement could be recorded real-timely during the loading-unloading process. Oliver-Pharr theory was adopted to calculate the contact area, by which the film hardness and elastic modulus could be obtained. Traditionally indentation depth was chosen less than 10% of film thickness to avoid substrate influence, but the choice is not universal and reasonable. G200 equipped with continuous stiffness measurement (CSM) technique could dynamically obtain film hardness H_f and reduced Young′s modulus E_r [9] and this can effectively avoid substrate effect.

The relationship among E_r, film Young′s modulus E_f and Poisson ratio v_f could be illuminated by following formula[10]:

$$\frac{1}{E_r}=\frac{(1-v_f^2)}{E_f}+\frac{(1-v_{\text{in}}^2)}{E_{\text{in}}} \tag{1}$$

Where E_{in} and v_{in} represent Young′s modulus and Poisson′s ratio of diamond indenter.

1.3 Thermoelastic characterization

Film stress σ is composed by internal stress σ_i and thermal stress σ_T. Film internal stress is only associated with film structure and the film-substrate interface state, independent of temperature. And assuming that the film Young′s modulus E_f and coefficient of expansion α_f are independent of temperature when the temperature changes little, then the change of σ as a function of temperature T can be given by the following expression:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}T}=\left(\frac{E_f}{1-v_f}\right)(\alpha_s-\alpha_f) \tag{2}$$

Where α_s and α_f respectively represent the coefficient of thermal expansion of substrate and film.

Double-substrate method[11] was taken to study thermoelastic characteristics of annealed SiO_2 films. The coated substrates surface profiles could be measured by Zygo GPI XP laser interferometer and the variation of film stress can be obtained by Stoney formula:

$$\sigma=\frac{E_s d_s^2}{6(1-v_s)d_f}\left(\frac{1}{R_f}-\frac{1}{R_0}\right) \tag{3}$$

Where d_s and d_f are the thickness of the substrate and the film, R_0 and R_f are substrate curvature before and after deposition. The samples were heated from room temperature, and surface profile were measured after every 10 ℃ increase. In order to make sure the sample reached thermal equilibrium, samples should be measured after temperature maintained for 20 min.

If SiO_2 films prepared on two different substrates, film thermal expansion coefficients α_f could be described as

$$\alpha_f=\frac{\alpha_{s2}\frac{\mathrm{d}\sigma_1}{\mathrm{d}T}-\alpha_{s1}\frac{\mathrm{d}\sigma_2}{\mathrm{d}T}}{\frac{\mathrm{d}\sigma_1}{\mathrm{d}T}-\frac{\mathrm{d}\sigma_2}{\mathrm{d}T}} \tag{4}$$

Where α_{s1} and α_{s2} are the thermal expansion coefficients of the two substrates.

And then SiO_2 film Poisson′s ratio and Young′s modulus could be calculated from formula(1), (2) and (4), shown as follows:

$$v_f=\left(\frac{1}{E_r}-\frac{(1-v_{\text{in}}^2)}{E_{\text{in}}}\right)\frac{\mathrm{d}\sigma}{\mathrm{d}T}\frac{1}{\alpha_s-\alpha_f}-1 \tag{5}$$

$$E_f=\frac{\frac{\mathrm{d}\sigma_1}{\mathrm{d}T}-\frac{\mathrm{d}\sigma_2}{\mathrm{d}T}}{\alpha_{s1}-\alpha_{s2}}\cdot\left[2-\left(\frac{1}{E_r}-\frac{(1-v_{\text{in}}^2)}{E_{\text{in}}}\right)\frac{\mathrm{d}\sigma}{\mathrm{d}T}\frac{1}{\alpha_s-\alpha_f}\right] \tag{6}$$

2 Results and discussions

2.1 Mechanical properties

Figure 1 shows the relationship between reduced Young′s modulus E_r and indentation depth of 350 ℃ annealed SiO_2 film deposited on Si<110>. By zooming in it can be seen that a "platform" comes forth while the indenter pushing down 35 nm into the film. And then E_r increases linearly with the indentation depth, illuminating that Si substrate character is showing up. So E_r of this SiO_2 sample could be exactly fixed on 69.5 GPa by continuous stiffness measurement.

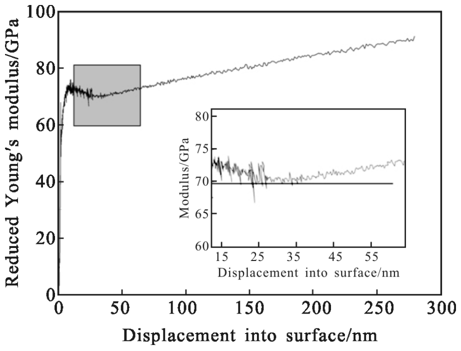

Fig.1 Reduced modulus with indentation depth

To eliminate systemic and random error and accurately obtain film mechanical parameters, every sample was measured times and E_r of sample could be calculated by averaging every "platform" value.

In Fig.2, the hardness values of the film sample mentioned above is plotted as a function of displacement into surface. The "platform" shows up at around 150 nm, and as the load increased, film hardness begins to reduce, indicating substrate effect. And also the sample should be measured times to obtain film hardness accurately. The results show well repeatability, and the average values of E_r and H are calculated as 68.6 GPa and 8.5 GPa.

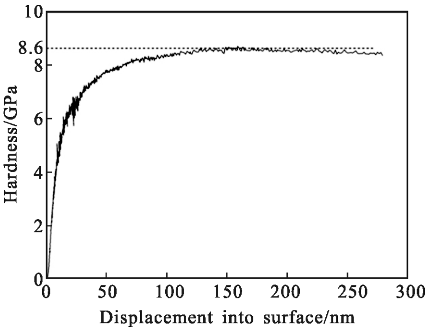

Fig.2 Film hardness with indentation depth

Reduced Young′s modulus and hardness of annealed samples are illustrated in Fig.3 and Fig.4, showing that E_r and H increase with T_a. E_r of samples on fused silica increases dramatically from 65.3 GPa to 71.7 GPa while T_a changing from 350 ℃ to 550 ℃. E_r of samples on Si<110> increases almost linearly while T_a is below 550 ℃, and it increases abruptly from 70.2 GPa to 80.4 GPa while T_a increasing to 750 ℃. H of samples on Si and silica has the same trend, which increases distinctly while T_a increasing from 350 ℃ to 550 ℃, and the change becomes gently while T_a is above 550 ℃.

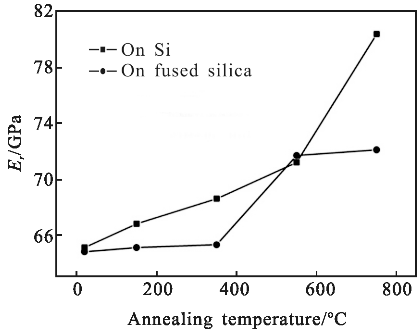

Fig.3 E_r of annealed films with T_a

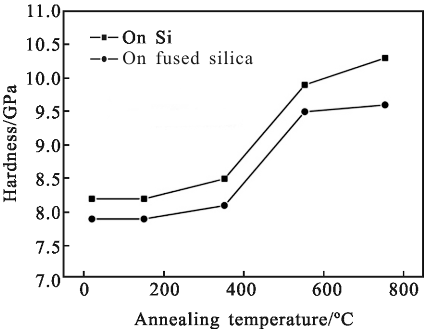

Fig.4 H of annealed films with T_a

It can also be seen that E_r and H of films on Si are generally larger than that on silica annealed at the same T_a. That may be because (1) Young′s modulus for Si and Silica are 112 GPa and 72 GPa, substrate effect could impact the test results; (2) while annealed at 750 ℃, ~60 nm oxide layer (TO−SiO_2) was created between Si substrate and SiO_2 film, which may cause the increase of film rigidity. So it can be concluded that Young′s modulus and hardness of SiO_2 films could be elevated by annealing.

2.2 Thermoelastic properties

Substrate profiles are measured by Zygo GPI XP interferometer. If the coating area is considered approximately spherical, according to Stoney formula, film stress change could be calculated by analyzing the change of substrate curvature after deposition or annealing.

It can be seen from Fig.5 and Fig.6 that SiO_2 films deposited by DIBS show compressive stress with little discreteness, and average stress on the two kinds of substrate is −415 MPa and −640 MPa separately. Stress change of annealed films could be obtained by deducting substrates change during the process. The compressive stress is released in certain extent after annealing according to the figures. The decrease of stress is almost linear with the increase of T_a below 450 ℃, and the stress change on silica is more obvious than that on Si. The stress release on Si reaches the maximum (366 MPa) while annealed at 550 ℃. Stress on silica becomes gentle while T_a is over 450 ℃ and it even changes from compressive stress to tensile stress while annealed over 450 ℃ on silica, for example, film stress (annealed at 550 ℃) changes from −606 MPa to 61.7 MPa.

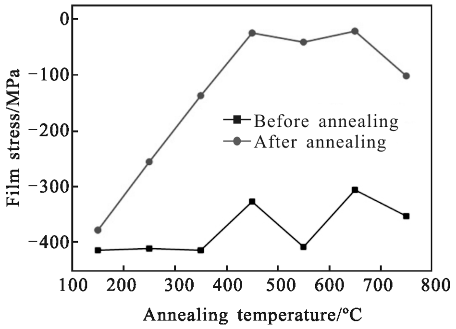

Fig.5 Stress change before and after annealing on Si substrate

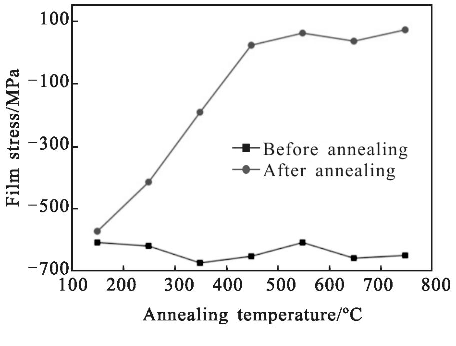

Fig.6 Stress change before and after annealing on silica substrate

The thermoelastic properties of SiO_2 films were studied by double-substrate method as mentioned before. Film (annealed at 550 ℃) stress change as function of heating temperature is shown in Fig.7. It can be seen that the dependence of σ on T is nearly linear, indicating that $d\sigma/dT$ is constant, independent of temperature.

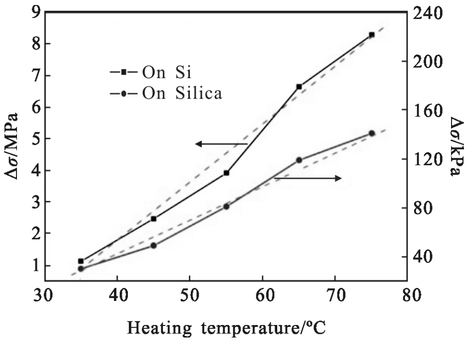

Fig.7 Stress change with heating temperature

Thermal expansion coefficient of film α_{f550} = 5.22×10^{-7} K^{-1}, calculated from formula (4) (where α_{si}= 2.62×10^{-6} K^{-1}, $\alpha_{silica}=5.55\times10^{-7}$ K^{-1}). Further the Poisson′s ratio and Young′s modulus could be obtained according to formula (5) and (6), v_{f550}=0.18, E_{f550}=152 GPa (where E_{in}=1 141 GPa and v_{in}=0.07).

The thermoelastic parameters of annealed SiO_2 films are shown in Tab.2. It can be seen that the influence of annealing process on v_f of SiO_2 films is not obvious, but E_f increases with annealing temperature, indicating the increase of film stiffness, and E_f is larger than Young′s modulus of silica. α_f of film reaches the minimum at 550 ℃ (5.22×10^{-7} $℃^{-1}$), which is smaller than that of silica.

Tab.2 Thermoelastic parameters of SiO_2 films annealed at different temperatures

	20 ℃	150 ℃	350 ℃	550 ℃	750 ℃	Silica
E_f/GPa	116	139	145	152	170	78
α_f/$℃^{-1}$	6.78×10^{-7}	6.35×10^{-7}	5.51×10^{-7}	5.22×10^{-7}	5.69×10^{-7}	5.5×10^{-7}
v_f	0.15	0.18	0.17	0.18	0.21	0.17

3 Conclusions

Mechanical and thermoelastic characteristics of

SiO_2 films prepared by dual ion beam sputtering were analyzed. The films were annealed in the atmosphere, and annealed temperature were chosen from 150 ℃ to 750 ℃. Reduced Young′s modulus and hardness of SiO_2 films were measured by continuous stiffness method, which could effectively avoid the substrate-effect. Films stress was calculated by analyzing substrate curvature change measured by laser interferometer. The thermoelastic properties of films were studied by double-substrate method (films were deposited on fused silica and Si<110>). The results show that E_r and H increase with annealing temperature, and which could be elevated from ~65 GPa to over 72 GPa and from ~8 GPa to ~10 GPa respectively after 750 ℃ annealing. The as-deposited SiO_2 films by DIBS showed compressive stress, and the stress could be released by annealing, even changing from compressive stress to tensile stress while annealing over 450 ℃ on silica, and the stress change on silica is more obvious than that on Si. Poisson′s ratio of annealed SiO_2 film is almost the same as fused silica, and E_f of films increased from 116 GPa to 170 GPa while annealing at 750 ℃. α_f of film reached the minimum (5.22×10^{-7} ℃$^{-1}$) while annealed at 550 ℃.

References:

[1] Liu Huasong, Wang Lishuan, Jiang Yugang, et al. Adjustments of refractive index and stress of SiO_2 films prepared by IBS technology [J]. ***Optics and Precision Engineering***, 2013, 21(9): 2238-2243. (in Chinese)

[2] Zhang Jinsheng, Zhang Jinlong, Ning Yongqiang, et al. Design and optimization of 1 555 nm broad-bandpass filter film[J]. ***Chinese Optics***, 2013, 21(9): 557-562. (in Chinese)

[3] Ma Hongping, Cheng Xinbin, Zhang Jinlong, et al. Damage growth characteristics of artificial nodules prepared by different processes [J]. ***Infrared and Laser Engineering***, 2017, 46(5): 0521001. (in Chinese)

[4] Lu J Y, Zhao Q N, Hou S H, et al. Study on antireflection of TiO_2-SiO_2/SiO_2 double-layer films prepared by sol-gel method[J]. ***Adv Mater Res***, 2012, 591-593:1012-1016.

[5] Cai Xikun, Zhang Lichao, Shi Guang, et al. Low stress DUV optical coatings deposited by ion beam sputtering [J]. ***Chinese Optics***, 2016, 9(6): 649-655. (in Chinese)

[6] Liu Huasong, Jiang Chenghui, Wang Lishuan, et al. Effects of annealing on properties of Ta_2O_5 thin films deposited by ion beam sputtering [J]. ***Optics and Precision Engineering***, 2014, 22(11): 2645-2651. (in Chinese)

[7] Jiang Yugang, Wang Lishuan, Liu Huasong, et al. Analysis on effects of thermal treatment on refractive index and absorption properties of SiO_2 film [J]. ***Infrared and Laser Engineering***, 2014, 43(4): 3334-3337. (in Chinese)

[8] Ji Yiqin, Jiang Yugang, Liu Huasong, et al. Analysis on effects of thermal treatment on structural characteristic of ion beam sputtering SiO_2 films [J]. ***Infrared and Laser Engineering***, 2013, 42(2): 418-422. (in Chinese)

[9] Zhou B, Prorok B C. A new paradigm in thin film indentation [J]. ***J Mater Res***, 2010, 25: 1671-1678.

[10] Klemberg-Sapieha J E, Oberste-Berghaus J, Martinu L, et al. Mechanical characteristics of optical coatings prepared by various techniques: a comparative study [J]. ***Appl Opt***, 2004, 43: 2670-2679.

[11] Thielsch R, Gatto A, Kaiser N. Mechanical stress and thermal-elastic properties of oxide coatings for use in the deep ultraviolet spectral region[J]. ***Appl Opt***, 2002, 41: 3211-3217.