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NH_3/HTMS 气相法改性 SiO_2 增透膜的耐环境稳定性

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摘　要: 溶胶–凝胶法制备的二氧化硅增透膜因具有极低的折射率与较高的激光损伤阈值而被广泛应用于高功率激光系统中。但是, 激光系统工作环境中的水汽及挥发性有机污染物极易污染薄膜。本研究以正硅酸四乙酯为前驱体, 氨水为催化剂, 乙醇为溶剂制备了碱性催化的单分散 SiO_2 溶胶。采用提拉法在 BK7 玻璃基板表面镀制了 SiO_2 薄膜, 并对薄膜进行氨水气氛以及 HTMS 气氛联合处理改性。改性后的薄膜表现出了极佳的耐环境稳定性, 在高湿环境下放置 2 个月后膜层峰值透过率仅下降 0.03%, 在低真空二甲基硅油污染环境下放置 2 个月后透过率光谱几乎无变化。NH_3/HTMS 气相法联合处理可以有效延长 SiO_2 增透膜在高功率激光系统中的工作寿命。

关　键　词: 溶胶–凝胶; 耐环境稳定性; 增透膜; 气氛处理

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Environmental Stable SiO_2 Antireflective Coating Modified *via* NH_3/HTMS Vapor Phase Treatment

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Abstract: Sol-Gel derived silica antireflective coatings have been widely used in high power laser system because of their ultra-low refractive index and high laser damage threshold. However, water vapor and volatile organic compounds in the laser system contaminate these coatings and reduce their antireflective efficiency and laser damage resistance. In this work, environmental stable SiO_2 antireflective coating was prepared by vapor phase treatment of ammonia and HTMS. Monodisperse colloidal silica sol was synthesized by Sol-Gel method using tetraethylorthosilicate (TEOS) as precursor, ammonia as catalyst, and ethanol as solvent. The silica coatings were then deposited on the BK7 glass using dip-coating method. Ammonia vapor phase treatment and HTMS vapor phase treatment were combined to improve the environmental stability of the antireflective coating. The peak transmittance of the BK7 glass coated with the modified coating decreased only 0.03% after being exposed in the humid environment for 2 m. Meanwhile, the transmittance curve of the BK7 glass coated with modified coating had almost no change after being placed under low vacuum condition with oil pollutants for 2 m, indicating that the coating modified *via* combined vapor phase treatment of ammonia and HTMS possessed an excellent environmental stable performance.

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Therefore, the combination of ammonia and HTMS vapor phase treatment is effective to improve the working life of SiO_2 antireflective coating in high power laser system.

Key words: Sol-Gel; environmental stability; antireflective coating; vapor phase treatment

高功率激光系统的发展推动了与之相适应的光学元件技术的研发。激光每通过一个光学元件的前后表面, 就会产生大约8%的能量损失。通过数百件甚至数千件光学元件之后, 其能量损失将十分严重[1]。基于溶胶–凝胶技术制备的 SiO_2 薄膜具有折射率可调、结构可控、激光损伤阈值高且易于在大尺寸不规则基板上镀膜等特性[2], 因此在高功率激光系统用大口径光学元件上得到了广泛应用与研究。采用 Stöber 法[3]制备二氧化硅溶胶并在光学元件上镀制的增透膜可以有效减少光能量损失, 并具备极高的激光损伤阈值。这种增透膜的纳米多孔特性使整个体系具有较高透过率, 但同时也限制了膜层的耐环境稳定性[1]。此外, SiO_2 粒子表面存在的大量羟基致使薄膜更加容易吸附环境中的极性污染物分子, 导致膜层透过率下降, 使用寿命严重缩短, 无法达到高功率激光系统的使用要求。因此, 在膜层使用前必须对其进行适当的处理, 以满足使用环境的需求。

目前, 对于增透膜的改性手段主要分为溶胶改性和薄膜表面后处理两种[4]。溶胶改性从溶胶合成机理出发, 在溶胶老化阶段引入相应的官能团取代羟基, 在 SiO_2 颗粒表面形成一个能阻挡污染物的外壳, 并使得颗粒间编织更加紧密, 从而达到有效抵抗外界环境污染物的效果。近年来通过在 SiO_2 溶胶中添加全氟硅烷[5-9]、有机硅烷[10-18]或有机聚合物[19-20]等改性方式来提高薄膜的耐候性。而薄膜表面后处理是通过向膜层表面引入相应官能团, 覆盖在 SiO_2 颗粒堆积成的薄膜表面, 也相当于编织成一个抗污染外壳, 对薄膜进行有效地保护, 从而由外向内改善薄膜特性。表面后处理方法操作简便, 薄膜的化学组成可以通过与多种不同的有机硅共同反应来调控, 也易于对高功率激光系统中大尺寸光学元件进行处理。与溶胶改性方法相比, 表面后处理法具有以下优势[21]: ①只有纯净的气态物质才会与薄膜表面接触, 进而对薄膜进行修饰, 很大程度上减少了其它大分子杂质对薄膜的影响; ②只有对薄膜进行完全表面修饰所需要的物质会参与其中, 避免了任何未参与反应的物质残留在薄膜表面, 使得薄膜表面修饰程度达到最大化。徐耀[22-25]、霍艳芳[26]和沈军[27-28]等课题组使用氨水与有机硅烷或与全氟硅烷气氛联合处理薄膜, 获得了单一环境下具有良好耐环境稳定性的增透膜。十六烷基三甲氧基硅烷(HTMS)作为一种表面处理剂, 易水解形成十六烷基硅醇, 将其长链烷烃结构接枝在 SiO_2 薄膜表面, 可以降低薄膜的表面能, 从而提高其耐环境稳定性。本工作通过氨水气氛处理和 HTMS 气氛处理联合使用, 成功制备了在高湿环境与低真空二甲基硅油污染环境下具有良好耐环境稳定性的增透膜。

1 实验方法

1.1 单分散 SiO_2 溶胶的制备

以正硅酸四乙酯(TEOS)为前驱体, 氨水为催化剂, 无水乙醇(EtOH)为溶剂, 制备单分散 SiO_2 溶胶。将 TEOS、EtOH 和氨水按照摩尔比为 1 : 40 : 2 混合搅拌 2 h, 然后在稳定环境(温度 20~25℃, 相对湿度<50%)下静置老化 7 d。待溶胶呈淡蓝色乳胶状后, 在 80℃下回流数小时, 去除溶胶中的催化剂氨, 从而得到稳定的 SiO_2 溶胶。

1.2 SiO_2 光学增透膜的制备

在相对湿度小于 50%的环境下, 采用 CHEMAT DIP MASTER 200 浸渍–提拉镀膜机, 以 100 mm/min 的提拉速度在清洁的 BK7 玻璃和单晶硅基底上分别镀制薄膜。将镀膜后的基底放入马弗炉中 80℃热处理 2 h, 得到的薄膜样品标记为 Base-SiO_2。

1.3 增透膜的 NH_3/HTMS 气氛处理

图 1(a)为 NH_3 气氛处理过程: 将含有氨水的培养皿放入密闭的 50℃恒温箱内, 薄膜样品直立在培养皿四周, 对其进行氨水气氛处理。6 h 后取出薄膜样品, 并用氮气吹掉表面残余气氛杂质, 所得薄膜样品标记为 NH_3-6h-SiO_2。

图 1(b)为 HTMS 气氛处理过程: 将 HTMS 与含有氨水的培养皿同时放入 50℃密闭恒温箱内, 进行 HTMS 的 NH_3 预处理。6 h 之后取出含有氨水的培养皿, 将薄膜样品直立在 HTMS 培养皿四周进行 HTMS 气氛处理 12 h, 最后取出薄膜样品并用氮气吹掉表面残余气氛杂质。

实验采用两步气氛处理薄膜: 先对提拉法制备的薄膜样品进行 6 h 的氨水气氛处理(与此同时对 HTMS 进行 6 h 的 NH_3 预处理)。随后将处理过的薄膜样品取出, 置于 NH_3 预处理过的 HTMS 中进行 12 h 的 HTMS 气氛处理, 得到的薄膜样品标记为 NH_3-6h-HTMS-12h-SiO_2。

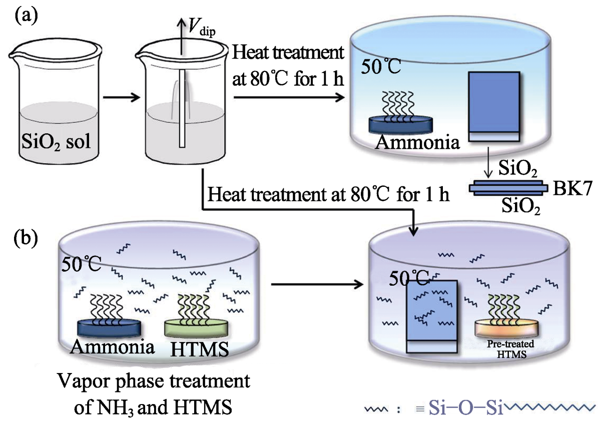

图 1　二氧化硅薄膜的氨水(a)和 HTMS(b)气氛处理示意图

Fig. 1　Diagram of SiO_2 coating modified *via* (a) ammonia vapor phase treatment and (b) HTMS vapor phase treatment

1.4　性能表征

采用紫外–可见–近红外分光光度计(JASCO V-570)测量薄膜的透射率光谱，入射角为 0°；使用傅里叶变换红外光谱仪(FT-IR, TENSOR Bruker 27)测量薄膜在 700~4000 cm^{-1} 的 FT-IR 图谱；使用扫描电子显微镜(SEM, Philips-XL30FEG)观测薄膜的表面和截面微观结构；利用 Film Wizard 软件对透过率与反射率拟合计算得到薄膜的折射率与厚度。

2　结果与讨论

2.1　NH_3/HTMS 气氛处理原理

图 2(a)为氨水气氛处理的原理示意图。前驱体正硅酸四乙酯在碱性催化条件下水解缩聚形成 SiO_2 颗粒的胶体镀膜液，颗粒的表面被大量羟基覆盖。镀膜过程中，颗粒沉积在基底表面，溶剂挥发后形成具有大量孔隙的 SiO_2 薄膜。经氨水气氛处理后，未水解的残留有机物进一步发生水解缩聚，同时 SiO_2 颗粒之间通过表面羟基脱水缩合，形成强化学键交联。在此过程中，SiO_2 颗粒发生 Ostwald 熟化[29]，小颗粒逐渐被大颗粒“吞噬”，形成更大的颗粒，颗粒之间以强化学键交联，从而使薄膜的耐摩擦性能和附着力得到大幅提高。图 2(b)所示为 HTMS 气氛处理原理示意图。HTMS 由一端为甲基的十六烷基有机长链和三个甲氧基构成。在氨水气氛预处理过程中，HTMS 发生水解反应生成大量硅羟基。在对 SiO_2 薄膜进行气氛处理时，可与 SiO_2 膜层表面的极性羟基基团发生缩聚反应，从而将 HTMS 的长链官能团接枝到二氧化硅颗粒的表面。这些非极性的长链结构，在二氧化硅颗粒的表面形成一层薄薄的保护层来阻止外来污染物侵入，进而增加薄膜的耐候性。

2.2　NH_3/HTMS 气氛处理薄膜的红外光谱分析

图 3 所示为氨水气氛处理以及 NH_3、HTMS 联合气氛处理的薄膜样品 FT-IR 图谱，从图中可以发现，所有样品的红外光谱在 800 和 1166 cm^{-1} 附近都出现了对应于 Si–O–Si 键的对称伸缩和反对称伸缩振动吸收峰[30]。2983 cm^{-1} 附近的吸收峰可能来源于溶胶中的有机残余物(乙醇或未水解的 TEOS)[31]，经过氨水气氛处理 6 h 后发生进一步水解–缩聚而消失。950 cm^{-1} 附近对应于 Si–OH 键伸缩振动的吸收峰，在 NH_3 气氛处理 6 h 后强度增强，而经过 HTMS 气氛处理 12 h 后强度又明显减弱，说明 HTMS 中的长链硅烷基替代了部分 SiO_2 颗粒表面的羟基亲水基团。经过 NH_3/HTMS 气氛联合处理后，在 1462 cm^{-1}

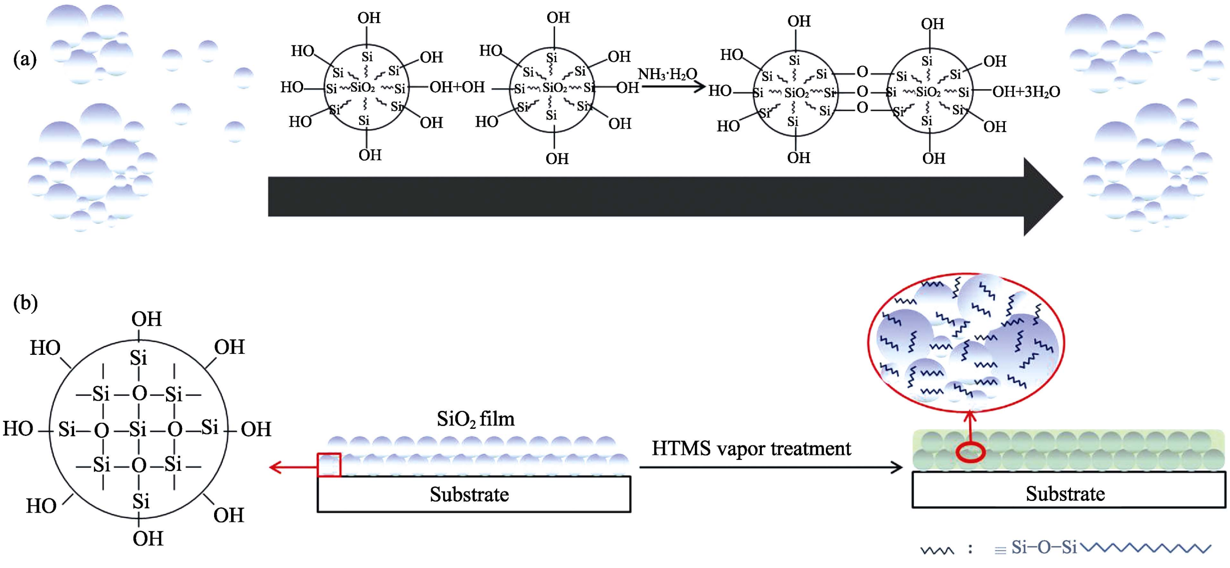

图 2　二氧化硅薄膜的氨水(a)和 HTMS(b)气氛处理原理示意图

Fig. 2　Schematic diagram of SiO_2 coating modified *via* (a) ammonia vapor phase treatment and (b) HTMS vapor phase treatment

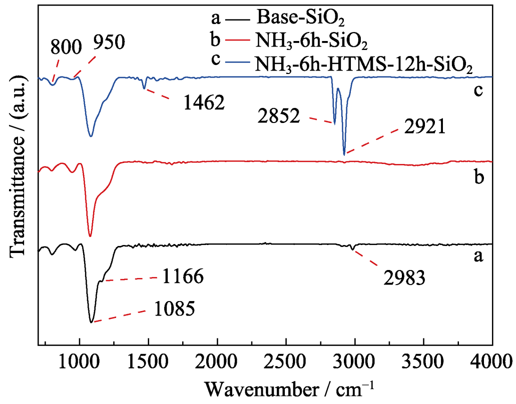

图 3 未经气氛处理(Base-SiO_2)、氨水气氛处理 6 h(NH_3-6h-SiO_2)以及 NH_3/HTMS 气氛联合处理(NH_3-6h-HTMS-12h-SiO_2)的薄膜样品红外光谱图

Fig. 3 FT-IR spectra of unmodified SiO_2 coating (Base-SiO_2), SiO_2 coating modified *via* ammonia vapor phase treatment (NH_3-6h-SiO_2) and NH_3/HTMS vapor phase treatment (NH_3-6h-HTMS-12h-SiO_2)

出现的吸收峰对应于次甲基的弯曲振动，2852、2921 cm^{-1} 处出现的吸收峰对应于亚甲基和甲基的对称伸缩振动和反对称伸缩振动[32]。这进一步说明气氛处理后的 SiO_2 薄膜表面存在着长链硅烷结构。

2.3 NH_3/HTMS 气氛处理薄膜的 SEM 结构分析

图 4 为未经气氛处理(a)、氨水气氛处理 6 h(b)以及 NH_3/HTMS 气氛联合处理(c)的薄膜样品 SEM 表面与截面照片。由表面照片可见，薄膜经过氨水气氛处理后孔洞有所增大，这是由于薄膜颗粒发生 Ostwald 熟化导致薄膜表面形成了更大的孔洞。而经过 HTMS 气氛处理后薄膜增加了一层含有长链基团的保护层，致使薄膜表面变得较为致密。截面形貌图也显示，未气氛处理的薄膜经过氨水气氛处理薄膜有所变薄并且略显致密，HTMS 气氛处理之后薄膜则变得更加致密，并且基底与薄膜的分界线越来越模糊。

2.4 NH_3/HTMS 气氛处理薄膜的光学性能分析

图 5 为未经气氛处理(Base-SiO_2)、氨水气氛处理 6 h(NH_3-6h-SiO_2)以及 NH_3/HTMS 气氛联合处理的薄膜样品(NH_3-6h-HTMS-12h-SiO_2)的透过率光谱图与折射率光谱图。由图 5(a)所示，二氧化硅薄膜透过率峰值未经气氛处理的为 99.20%，经氨水气氛处理 6 h 的达到 99.60%，而 NH_3/HTMS 气氛联合处理的达到 99.67%。相对于氨水气氛处理的薄膜，HTMS 气氛处理透过率光谱变化不大，说明 HTMS 气氛处理并未对薄膜透过率产生太大影响，依然能够保持较高的透过率。图 5(b)显示薄膜经过氨水气氛处理和 NH_3/HTMS 气氛联合处理后折射率均有所升高。而根据薄膜光学原理[33]，对于 BK7 玻璃基底而言，薄膜的折射率越接近 1.22，透过率越高，这与图 5(a)透过率光谱的结果一致。未经气氛处理(Base-SiO_2)、氨水气氛处理 6 h(NH_3-6h-SiO_2)以及 NH_3/HTMS 气氛联合处理的薄膜样品(NH_3-6h-HTMS-12h-SiO_2)的厚度分别为 126.6、112.4 和 114.7 nm。氨水气氛处理后薄膜的厚度减小，是 Ostwald 熟化使得薄膜结构收缩导致的。此外，NH_3/HTMS 气氛联合处理的薄膜只比氨水气氛处理的薄膜厚 2.3 nm，这进一步说明联合处理在薄膜表面形成的保护层很薄，基本不会影响薄膜的透过率。

2.5 NH_3/HTMS 气氛联合处理薄膜耐环境稳定性分析

图 6 为未经气氛处理的二氧化硅薄膜与 NH_3/HTMS 气氛联合处理的薄膜分别在潮湿环境(RH>90%)下以及低真空(≤10^{-3} Pa)二甲基硅油污染环境下存放 2 个月前后的透过率光谱图。在潮湿环境下，未经气氛处理的薄膜放置两个月后峰值透过率下降了约 0.56%，而经过 NH_3/HTMS 气氛联合处理后薄膜峰值透过率仅下降 0.03%。在低真空二甲基硅油环境下，未经气氛处理的薄膜经过 2 个月后虽然峰值透过率仅下降了约 0.09%，但是峰位发生了明显移动；而经过 NH_3、HTMS 气氛联合处理的薄膜透过率光谱几乎未发生变化，且峰位也未发生变化。以上结果表明，经 NH_3/HTMS 气氛联合处理后的增透膜的环境稳定性显著增强。

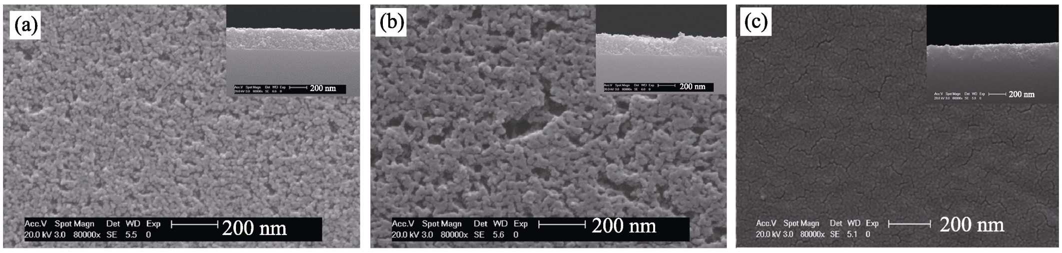

图 4 未经气氛处理(a)、氨水气氛处理 6 h(b)以及 NH_3/HTMS 气氛联合处理(c)的薄膜样品 SEM 表面与截面照片

Fig. 4 SEM surface and cross-section images of unmodified SiO_2 coating (a), SiO_2 coating modified *via* ammonia vapor phase treatment (b) and NH_3/HTMS vapor phase treatment (c)

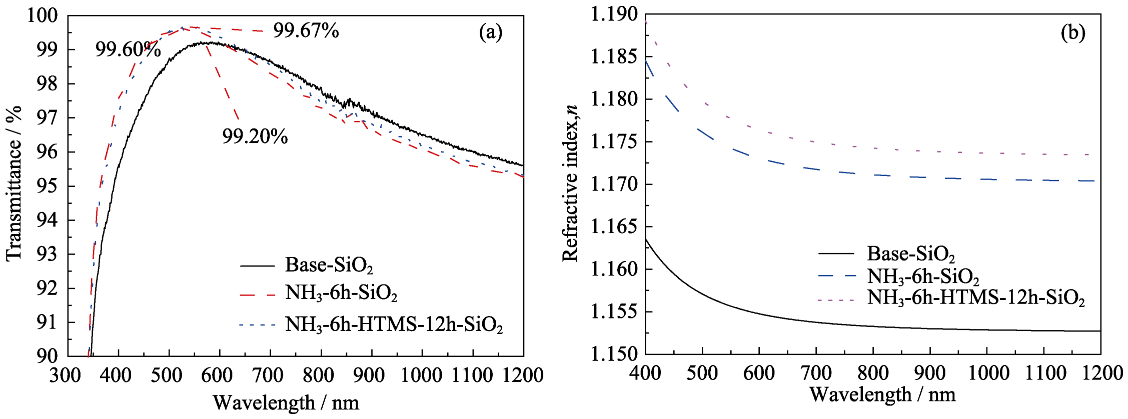

图 5　未经气氛处理(Base-SiO_2)、氨水气氛处理 6 h(NH_3-6h-SiO_2)以及经过 NH_3 和 HTMS 气氛联合处理的薄膜样品(NH_3-6h-HTMS-12h-SiO_2)的透过率光谱图(a)及其折射率光谱图(b)

Fig. 5　(a) Transmittance spectra and (b) refractive index spectra of unmodified SiO_2 coating (Base-SiO_2), SiO_2 coating modified *via* ammonia vapor phase treatment (NH_3-6h-SiO_2) and NH_3/HTMS vapor phase treatment (NH_3-6h-HTMS-12h-SiO_2)

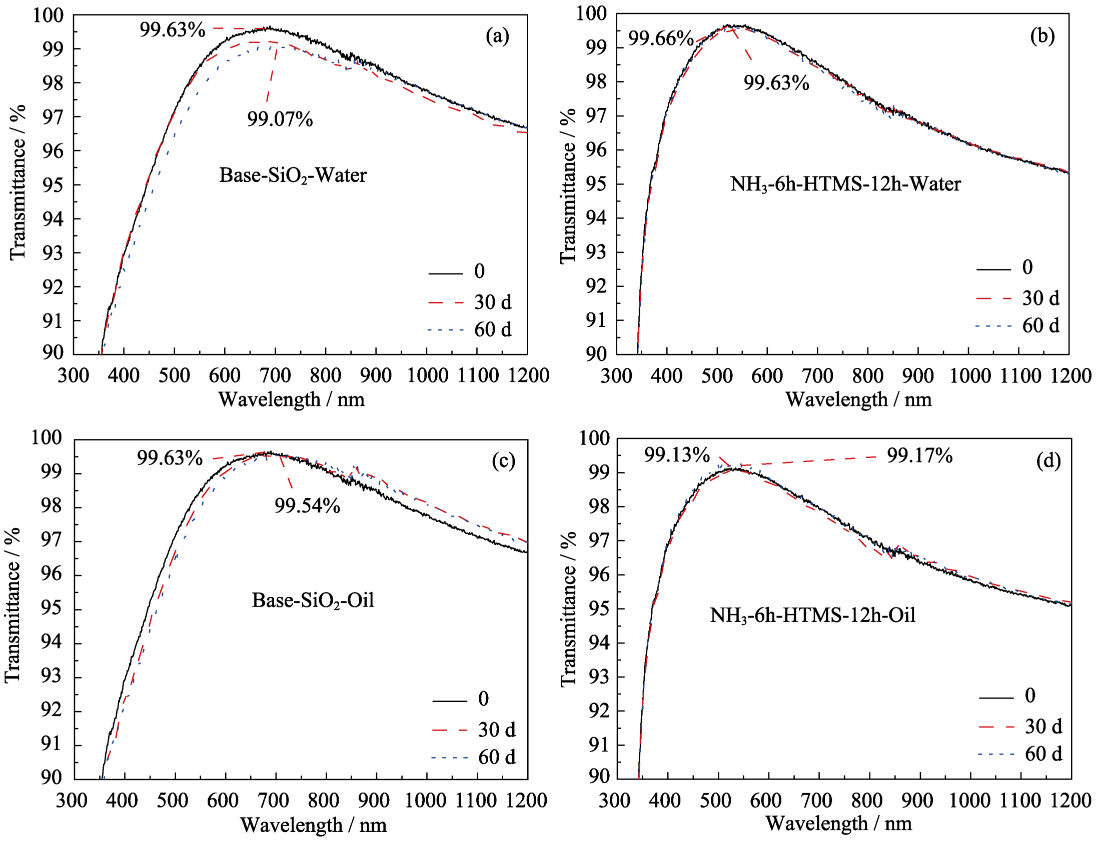

图 6　潮湿环境下(a)未经处理的和(b)NH_3/HTMS 气氛联合处理的二氧化硅薄膜透过率光谱图；低真空二甲基硅油环境下(c)未处理的和(d) NH_3/HTMS 气氛联合处理的二氧化硅薄膜透过率光谱图

Fig. 6　Transmittance spectra of (a) unmodified SiO_2 coating and (b) SiO_2 coating modified *via* NH_3/HTMS vapor phase treatment after being exposed in the humid environment; Transmittance spectra of (c) unmodified SiO_2 coating and (d) SiO_2 coating modified *via* NH_3/HTMS vapor phase treatment after being placed under low vacuum condition with oil pollutants

3　结论

本研究通过对 SiO_2 薄膜进行 NH_3/HTMS 气氛联合处理，即对薄膜先进行氨水气氛处理，再进行 HTMS 气氛处理，得到十六烷基长链官能团修饰的 SiO_2 增透膜。改性后的薄膜在潮湿环境及低真空二甲基硅油污染环境中均表现出良好的耐环境稳定性，同时保持了溶胶–凝胶 SiO_2 薄膜的高透过率。NH_3/HTMS 气氛联合处理的二氧化硅增透膜在潮湿环境下放置两个月透过率峰值仅下降 0.03%；在低真空二甲基硅油污染环境下同样放置两个月，薄膜

透过率光谱几乎未发生变化。

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