



# Improvement of the environmental stability of sol-gel silica anti-reflection coatings

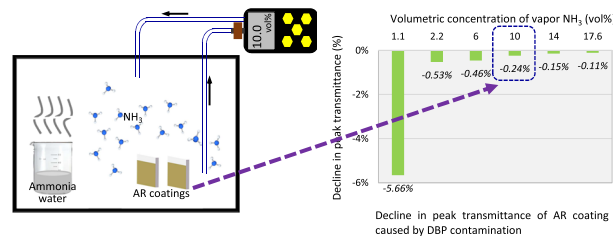
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## Abstract

The environmental stability of sol-gel anti-reflection (AR) coatings on optical components is improved by an exposition to volumetric concentrated ammonia vapors. Coatings of 86 nm thickness are prepared by dip-coating in the silica sol synthesized by hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in the ethanol solvents with a base catalyst. Due to the sol-gel process, the coatings have a large micro-porosity and consequently susceptible to contamination by adsorbing volatile organic compounds in the vacuum environment of high-powered lasers. The ammonia vapor ( $\text{NH}_3$ ) followed by hexamethyldisilazane (HMDS) vapor respectively at room temperature is used to reduce the susceptibility. This work presents how the concentration of  $\text{NH}_3$  vapor exposed to the coatings affects the environmental stability regarding to the optical performance, and shows that  $\text{NH}_3$  vapor treatment with volumetric concentration of at least 10 vol% can make the coatings substantially durable, combined with excess HMDS vapor treatment both for 24 h. Besides, different off-line methods of cleaning to remove the deposition of the vapor contamination within the coatings, including infrared heating, ethanol dipping, and plasma cleaning, are investigated and compared.

## Graphical abstract



**Keywords** Sol-gel anti-reflection coating · Environmental stability · Volumetric concentrated ammonia vapor · Vacuum contamination · Cleaning

## Highlights

- Compared the  $\text{NH}_3$  treatment alone and HMDS treatment alone to the sol-gel AR coating, proving  $\text{NH}_3$  treatment dominates the contamination resistance.
- Analyzed the effects of volumetric concentration of vapor  $\text{NH}_3$  treatment on the environmental stability of the sol-gel AR coatings systematically.
- The least volumetric concentration of  $\text{NH}_3$  vapor exposed to the sol-gel AR coating to achieve substantially environmental stability is 10 vol%.
- The effectiveness of three methods of off-line cleaning the contamination within the sol-gel AR coatings is verified.

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## 1 Introduction

Porous silica AR coatings prepared by sol-gel process have long been used in high-powered lasers owing to their high laser damage threshold. Due to the sol-gel process, the AR coating has a high specific surface area, and thus susceptible to vapor contamination from the vacuum environment in the lasers. Contamination by adsorption can cause the degradation of the optical performance, thus reducing the transmittance of the optics, and cause a great energy deposition from energy absorption, eventually damaging the coating as well as the optics. To address the problem, the post treatment to the coatings is developed and has been proved effective. That is to expose the coatings to vapor ammonia water and then to HMDS vapor respectively [1–3]. The vapor  $\text{NH}_3$  will cause a shrinkage of the coating by reducing the porosity, making the coatings tightly to prevent the macromolecules of contaminants [4, 5]. The HMDS vapor can further modify the coating surfaces with sufficient non-polar chemical radicals protecting from the polar groups like hydroxide radical [1, 6]. Although the vapor post-treatment to the coatings can greatly reduce the environmental contamination, the AR coatings are unlikely to survive when the environment in the lasers become very harsh or change greatly. While, the vapor contamination especially in the vacuum chambers cannot be avoided completely [2, 7]. That means more efforts are needed to improve the environmental stability and reduce the susceptibility of the AR coatings. To reach this goal, much efforts are made in aspect of post treatment, e.g., to change the HMDS to other kinds [8, 9], to change the treatment time [10], or to modify the sol components [11–15]. However, almost no reports focused on the effect of the volumetric concentration of the treatment vapor on the coating stability, especially about  $\text{NH}_3$ . Besides, When the AR coatings are badly contaminated, the on-line or off-line way of removal of the contaminants adsorbed may be beneficial, such as, laser cleaning [16], and plasma cleaning [17].

In this work, the relationship between the vapor concentration of  $\text{NH}_3$  and anti-contamination performance of the coatings is studied. It is observed that at least 10 vol% vapor  $\text{NH}_3$  can improve the environmental stability of the coating in the vacuum of the lasers effectively with respect to the transmittance. Besides, the comparison of different methods of off-line cleaning the coating, including ethanol flushing, infrared heating, plasma cleaning, is studied and the results show that these methods can all clean the contaminated coatings effectively, but the plasma cleaning could easily cause a decline in coating thickness. This work shows potential application in the high-powered lasers to promote the coated optical components service life, to

suppress the back stray light, and to save the operating costs as well.

## 2 Materials and methods

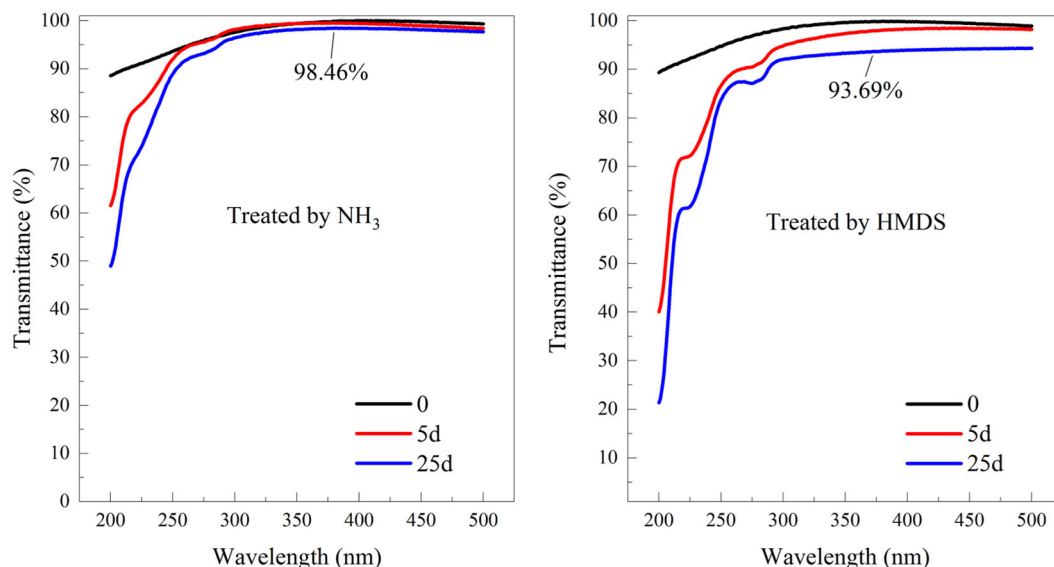
The coating suspension sol was prepared by the base catalyzed hydrolysis of TEOS (99%) in anhydrous ethanol (99.8%). The weight ratio of three reagents is sequentially 86.7% anhydrous ethanol: 2.9% ammonia water: 10.4% TEOS. The freshly mixed solution was set for 7 days at room temperature as the aging process. The particle size of  $\text{SiO}_2$  within the product sol is approximately 23.8 nm on average, which is measured by nanometer particle size meter (Zetasizer Nano ZS). The coatings were deposited via dip coating method on well-cleaned fused quartz substrates. The newly prepared AR coatings were then subjected to  $\text{NH}_3$  treatment with different vapor concentration for 24 h as the  $\text{NH}_3$  curing process, and then to HMDS (99%) vapor treatment for another 24 h. The vapor  $\text{NH}_3$  is from the volatilization of ammonia water (28 wt%). After the both vapor treatments, the AR coatings were transferred to a vacuum chamber for the contamination tests, in which a small beaker (7 mm diameter of opening) of DBP (99%) was set as the representative of the volatile organic compounds in the vacuum environment of high-powered lasers [18]. The vacuum is exhausted to  $10^{-3}$  Pa to accelerate the volatilization of DBP. The contamination test lasts for 35 days.

All the chemicals used are of analytical grade. An UV/VIS-NIR Spectrophotometer (Lambda 950, PerkinElmer) is utilized to measure the optical transmittance of the coated optical fused quartz substrate (50 mm × 50 mm × 4 mm). The speed of dip coating needs to be controlled precisely to make the peak position of the optical transmittance curve after post-treatment close to 351 nm or slightly less than 351 nm, since 351 nm is the typical wavelength of the 3W powered lasers. The peak of the transmittance curve between 200 nm to 500 nm of the coated sample was monitored to evaluated how much the vapor contamination affects the coating indirectly.

## 3 Results and Discussion

### 3.1 Comparison of single treatment

Figure 1 gives the contrast of the contamination resistance of the coatings treated by  $\text{NH}_3$  alone and HMDS alone, respectively. The coating treated by  $\text{NH}_3$  alone have a higher optical transmittance (98.46%) after 25 days contamination by DBP vapor at  $10^{-3}$  Pa than that treated by HMDS alone (93.69%), where the latter already lost the AR



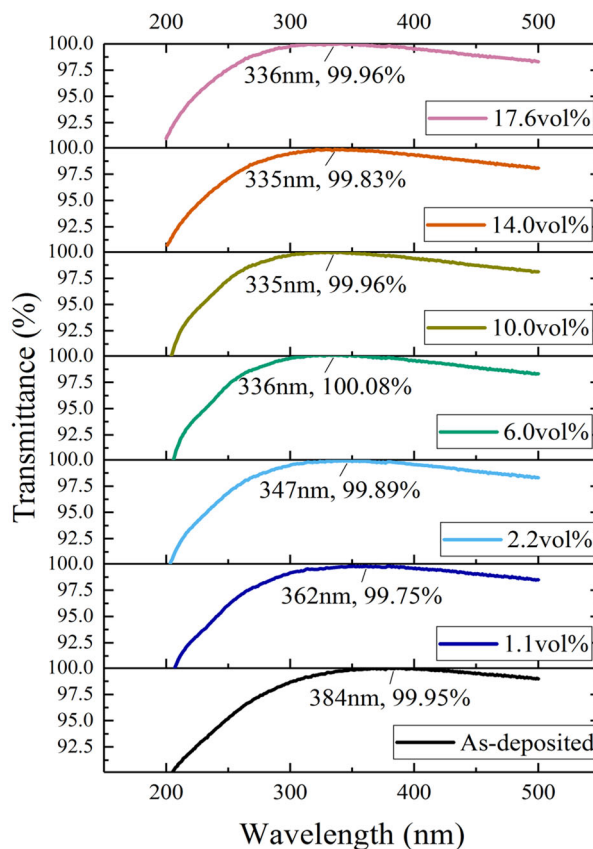
**Fig. 1** The properties of the contamination resistance of the coatings treated by  $\text{NH}_3$  alone (6.0 vol%) and HMDS alone, respectively

property. The transmittance of the coating treated by HMDS alone is contaminated more badly by DBP especially in the absorbing band between 200 nm to 300 nm, which means  $\text{NH}_3$  vapor could endow the coatings more resistance to the DBP than HMDS. That is to say, in the two procedures of the post treatment ( $\text{NH}_3$  plus HMDS),  $\text{NH}_3$  treatment dominates the contamination resistance property, indicating that increasing the treatment extent by  $\text{NH}_3$  may promote the coating contamination resistance more efficiently than that by HMDS.

### 3.2 Enhanced $\text{NH}_3$ treatment

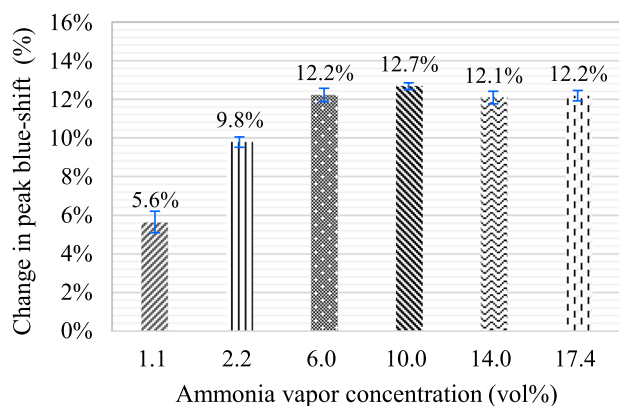
Figure 2 shows the change of the peak wavelength of the transmittance curve when the coatings were exposed to different volumetric concentration of the  $\text{NH}_3$  for 24 h. The wavelength peaks of the coatings as deposited are around 384 nm, which corresponds to a physical thickness of 86 nm of the AR coating when coated on the silicon wafer measured by spectroscopic ellipsometer (SE850, Sentech). The  $\text{NH}_3$  curing process causes a shrinkage of the coating which differs from the vapor concentration. The peak of the coating blue-shift with the rise of the  $\text{NH}_3$  vapor concentration when it is less than 6.0 vol% and does not blue-shift further when it is more than 6.0 vol%, which means a limitation of shrinkage exists during the  $\text{NH}_3$  curing of the AR coatings. All samples show rather high peak transmittance after  $\text{NH}_3$  vapor treatment, indicating that no peak transmittance was sacrificed during the  $\text{NH}_3$  curing process.

Figure 3 gives the statistics of the percentage of blue shifts of the coatings during the  $\text{NH}_3$  vapor treatment with different volumetric concentration. The average peak blue



**Fig. 2** The changes in the transmittance curves of the AR coatings during the curing process by different volumetric concentration of  $\text{NH}_3$

shift is 12.6% when the  $\text{NH}_3$  vapor concentration is between 6.0 vol% and 17.6 vol%, suggesting that the least  $\text{NH}_3$  volumetric concentration of 6.0 vol% could bring sufficient shrinkage of the AR coatings.

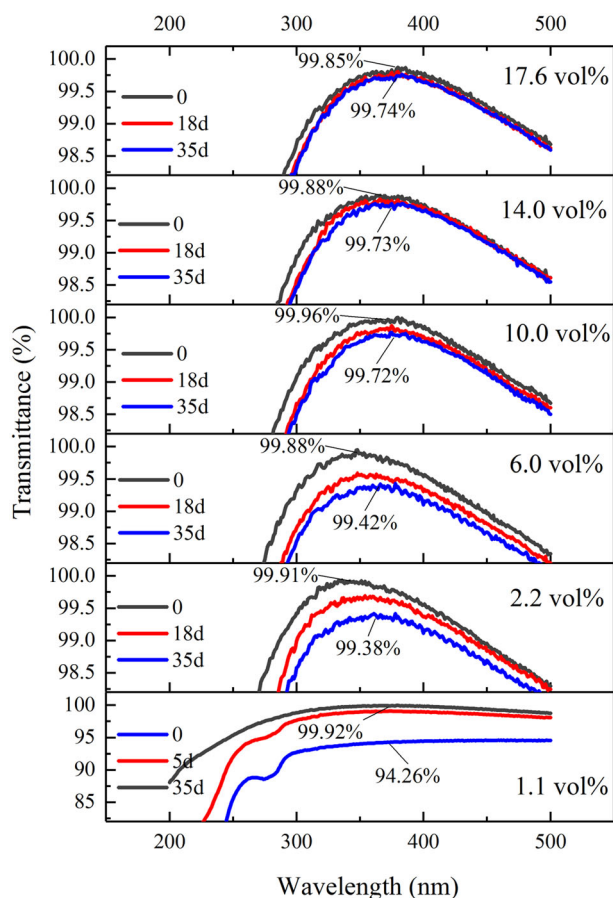


**Fig. 3** The changes in the ratio of peak blue-shift of the AR coatings during the curing process with different volumetric concentration of  $\text{NH}_3$

The  $\text{NH}_3$  vapor treatment is used to induce a hydrolysis of all the ethoxyl groups to hydroxyl groups with the formation of Si-OH groups and further condensation of some of the hydroxyl groups to Si-O-Si linkages [1]. The volatile organic vapor contaminant is adsorbed within the sol-gel coatings by pore adsorption type and surface type. The surface type takes place typically by polar groups of Si-OH interacted with the contaminant chemically. The pore adsorption type is typically of physical way. With the increase of the  $\text{NH}_3$  vapor concentration, the proportion of the residual Si-OH groups inside the coatings are reduced further due to more formation of the Si-O-Si linkages, causing more pores to contract and thus leading to less porosity and more coating shrinkage. However, no more Si-O-Si linkage forms when the  $\text{NH}_3$  vapor concentration is above 6.0 vol%, which is suggested in Figs. 2 and 3.

### 3.3 Contamination test

Figure 4 shows the transmittances of the coatings after 35 days' contamination of DBP. With the increase of the contamination time, the transmittances of all coatings declined. However, the transmittance of the coating treated by higher volumetric  $\text{NH}_3$  decreases less, meaning the coating becomes more contamination-resistant or environmentally stable. Table 1 gives the transmittances of the coating on every stage of post treatment and contamination test. Each data point was the average value of measurements for three times, with an error of 0.15%. The data show excellent contamination resistance or stability when the volumetric concentration of  $\text{NH}_3$  higher than 10.0 vol%. In comparison with Fig. 1, the enhanced concentrated  $\text{NH}_3$  treatment plus HMDS treatment is able to lead to environmentally stable AR coatings, resisting the volatile organic compounds in the vacuum environment of high-powered lasers.



**Fig. 4** The peak transmittances (%T) of the AR coatings after the contamination of 35 days

Theoretically, the concentrated vapor  $\text{NH}_3$  treatment can reduce the porosity and lower the adsorption within the coating dramatically. The HMDS causes substitution of the Si-OH groups on the surface by trimethylsiloxy groups, preventing the contaminant adsorbed on the surface of the coatings. The results of the contamination test given in Table 2 indicate that the treatment by  $\text{NH}_3$  vapor lower than 10.0 vol% is not sufficient for the contamination resistance. That means, the  $\text{NH}_3$  vapor treatment with the volumetric concentration of more than 10.0 vol% can make the coating substantially environmentally stable.

Compared with Figs. 2, 3 and 6 vol% concentrated  $\text{NH}_3$  vapor can readily cause the limitation of the shrinkage of the coatings, but the durable anti-contamination performance cannot be achieved until 10 vol%. That is to say, the limitation of the shrinkage by 6 vol% concentrated  $\text{NH}_3$  vapor primarily takes place among the  $\text{SiO}_2$  particles, and higher concentrated  $\text{NH}_3$  vapor than 6 vol% may causes condensation of the hydroxyl groups to Si-O-Si linkages on the surface of individual particle or within the individual particle. As a result, the micro pores or polar groups within the individual particle can be reduced. Therefore, increasing

**Table 1** The peak transmittances (%T) of the AR coatings during the stages of post treatment and contamination test<sup>a</sup>

NH <sub>3</sub> vapor concentration (vol%)	%T							
	As deposited		After NH <sub>3</sub>	After HMDS	After DBP contamination			Δ%T
	5d	18d	35d	5d	18d	35d		
1.1	99.92	99.93	99.92	99.05	95.09	94.26	5.66	
2.2	99.97	99.96	99.91	99.80	99.67	99.38	0.53	
6.0	99.89	99.92	99.88	99.70	99.57	99.42	0.46	
10.0	99.99	99.94	99.96	99.82	99.84	99.72	0.24	
14.0	99.99	99.91	99.88	99.82	99.80	99.73	0.15	
17.6	99.86	99.91	99.85	99.76	99.74	99.74	0.11	

<sup>a</sup>Δ%T means the peak transmittances before and after a 35 days' contamination test in DBP vapor, ΔT = %T (after HMDS) – %T (after 35 days' contamination)

**Table 2** The change of physical property of the coating by ammonia curing

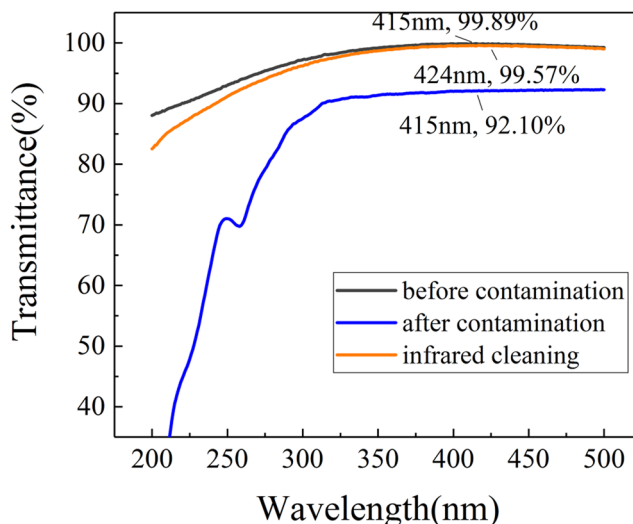
NH <sub>3</sub> vapor concentration (vol%)	As deposited			After NH <sub>3</sub> treatment			Change in thickness (%)	Change in Refractive index (%)	Change in Optical thickness (%)
	Thick-ness (nm)	Refractive index	Optical thickness n*d	Thick-ness (nm)	Refractive index	Optical thickness n*d			
1.1	81.57	1.206	98.37	80.42	1.196	96.18	-1.41	-0.84	-2.23
2.2	87.45	1.210	105.81	81.75	1.233	100.80	-6.52	1.90	-4.73
6.0	85.86	1.208	103.72	79.96	1.231	98.43	-6.87	1.90	-5.10
10.0	88.66	1.213	107.54	82.47	1.236	101.93	-6.98	1.90	-5.22
14.0	86.85	1.215	105.52	80.70	1.235	99.66	-7.08	1.65	-5.56
17.6	84.25	1.212	102.11	78.30	1.232	96.47	-7.06	1.65	-5.55

the concentration of the NH<sub>3</sub> vapor above 10 vol%, a continuing decline in the loss of peak transmittance of the coating can be obtained after 35 days contamination test, as illustrated in Fig. 4 and Table 2.

**3.4 Off-line cleaning**

As for the off-line methods of cleaning or removal of contaminants, Fig. 5 presents the effect of the infrared cleaning of the contaminated AR coating. The coating as deposited was treated by NH<sub>3</sub> vapor and later HMDS vapor. In order to be severely contaminated, the volumetric concentration of NH<sub>3</sub> during the post treatment is lower than 1.5 vol%. After contaminated, the coating lost the AR property. Then it was subjected to infrared heating for 20 min as the infrared cleaning. In Fig. 5, the cleaned coating has a peak transmittance of 99.57%, just slightly lower than 99.89% before contaminated. In spite of the separation between the two curves in the shorter wavelength, the infrared cleaning can effectively remove the DBP adsorbed within the coating.

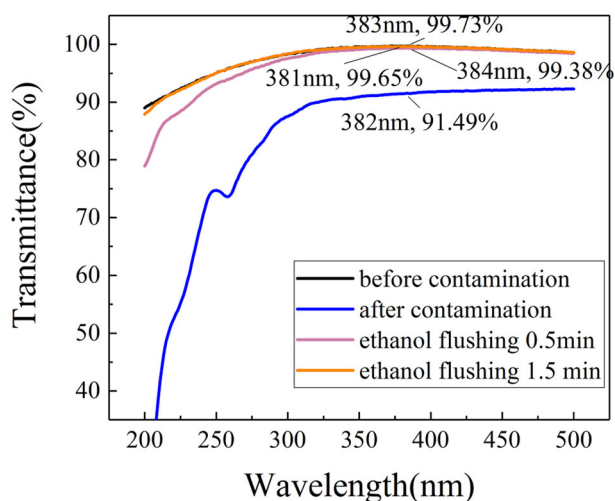
Figure 6 shows the effect of the ethanol flushing cleaning of the contaminated AR coating. After 2 cycles of ethanol flushing, the cleaned coating has a peak transmittance almost equal to that of the uncontaminated coating,



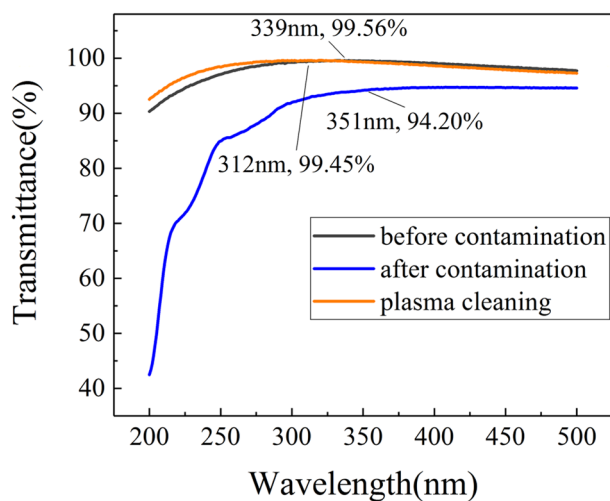
**Fig. 5** Infrared cleaning of the contaminated AR coating

indicating the effectiveness and briefness of such a cleaning method.

Figure 7 shows the cleaning of the AR coating by plasma. The plasma is generated by circuit at radio frequency of 20 kHz with a vacuum of approximately 30 Pa. The period of plasma cleaning lasts 5 min. In Fig. 7, the plasma cleaning can effectively remove the contaminants



**Fig. 6** Ethanol flushing cleaning of the contaminated AR coating



**Fig. 7** Plasma cleaning of the contaminated AR coating

and the peak transmittance can be almost recovered entirely. However, the plasma cleaning has a by-effect, i.e., a reduction in thickness of the coating or an obvious blue shift (27 nm) in the peak wavelength. This is mostly because the vacuum plasma accelerated by the electric field can bombard the surface of the coatings. To avoid it, the power of the plasma, the cleaning time and the degree of vacuum should be controlled precisely.

## 4 Conclusion

In summary, the enhanced vapor  $\text{NH}_3$  treatment has successfully improved the contamination resistance of the sol-gel AR coatings. The least volumetric concentration of 10 vol% is needed to make the coatings stable and durable when exposed to volatile organic compounds in the vacuum

environment of high-powered lasers. This is beneficial for the reduction in the damage of coated optics caused by contamination adsorption and deposition, and for the suppression of the stray light. In addition, the three off-line cleaning methods of contaminated AR coatings are compared and all prove effective, which could be applicable for the cycle-loop of optics.

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## Compliance with ethical standards

**Conflict of interest** The authors declare no competing interests.

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