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光学元件清洗过程中同步辐射活化氧的研究

钟鹏飞[1],周洪军[2],霍同林[2],张国斌[2],郑津津[1]
(1.中国科学技术大学 精密机械与精密仪器系,安徽 合肥 230027;
2.中国科学技术大学 国家同步辐射实验室,安徽 合肥 230029)

摘要:在同步辐射应用中,光学元件被污染是一个常见问题,而光学元件的污染会造成光通量的极大损失。为了有效地清洗光学元件,研究了清洗过程中的光化学反应,进行了氧气在同步辐射光作用下分解的实验。通过对实验中产生的气体成份分析,进行光化学反应研究。首先,测量通氧气时的气体成份;然后,测量通氧气和同步辐射光照时的气体成份。通过两者比较,分析氧气分解的情况。实验结果表明,氧分子在同步辐射光作用下发生分解,产生质量数为 16 的氧原子、氧离子和质量数为 48 的臭氧,它们的成份分别占 1%和 0.005%~0.01%。

关 键 词:同步辐射;活化氧;氧原子;臭氧
中图分类号:O432.1;O644.1 **文献标识码**:A

Research of oxygen activation by synchrotron radiation in optical component cleaning process

ZHONG Peng-fei[1], ZHOU Hong-jun[2], HUO Tong-lin[2],
ZHANG Guo-bin[2], ZHENG Jin-jin[1]

1. *Department of Precision Machinery and Precision Instrumentation, University of Science and Technology of China, Hefei* 230027, *China*;
(2. *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei* 230029, *China*)

Abstract: In order to optimize the optical component cleaning process, the oxygen dissociation by synchrotron radiation has been researched by analyzing the gas composition produced in cleaning process. The gas composition is measured by quadrupole mass spectra when synchrotron radiation light irradiates the oxygen filled in vacuum chamber. The gas composition and content can be established by analyzing the data gathered. Experimental results indicate that oxygen can be dissociated by synchrotron radiation light to produce some species with strong oxygenation, such as oxygen atom and ozone. The content of oxygen atom is about 1% and the content of ozone is about 0.005%~0.01% in cleaning process.

Key words: synchrotron radiation; activated oxygen; oxygen atom; ozone

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1 Introduction

Optical element surfaces get contaminated when they are exposed to synchrotron radiation light[1-4]. Contamination causes the reflectivity and transmittance of optical components to descend . Photon flux of photon energies above the C edge (280 eV) degrades severely. In order to refresh the contaminated optical components, much work has been done by synchrotron radiation (SR) laboratories worldwide[1-6]. Such techniques as in-situ optical component cleaning by plasma and RF (DC or AC) have been developed for this purpose. Some cleaning gases including H_2O, O_2, H_2O and O_2 mixture, C_2F_6 and O_2 mixture etc. are used for this purpose. Plasma or RF produces excited oxygen species, including single O atoms, ions ozone , and hydroxide radicals if there is water vapor. These species can react with carbon to form volatile species such as CO and CO_2, which is then pumped away.

Researchers have now found that contaminated optical elements can be refreshed in the cleaning ways mentioned above. However these cleaning methods have some drawbacks, for example, plasma discharging devices are difficult to design to avoid second contamination of electrodes effective cleaning and some special optical components necessitates complex design of reactor. A separate cleaning device must be designed for each element in beam lines. A long time is taken to bake synchrotron radiation apparatus after the cleaning to maintain vacuum.

William K. Warburton applied photon activated oxygen cleaning method to clean contaminated optical components[7]. Photons in the 10～1 000 eV range are well known to be capable of breaking molecular bonds[8] both on surfaces and in the gas phase. Synchrotron radiation light covers this energy range.

This article focuses on pure oxygen gas dissociation at different gas fluxes. The gas composition is monitored by quadrupole mass spectra (MKS, USA) under different experimental conditions in the cleaning process. Experimental results indicate the cleaning speed is proportional to oxygen pressure and illumination time of synchrotron radiation light.

2 Experiment approach

An experiment was carried out at the VUV Circular Dichroism Station in National Synchrotron Radiation Laboratory. Fig. 1 is a photo of the experimental set-up and Fig. 2 is a schematic diagram of the experimental set-up.

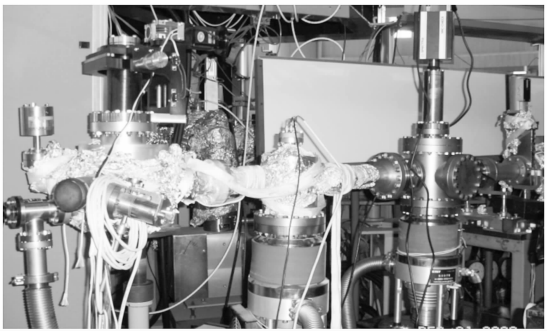

Fig. 1 Photo of experimental set-up

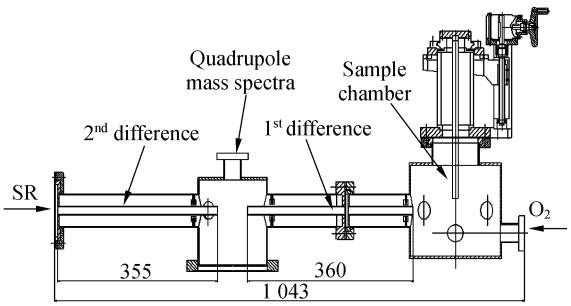

Fig. 2 Schematic diagram of the experimental set-up

The storage ring and beamline are working at 10^{-8} Pa pressure to obtain the long lifetime beam current. The cleaning experimental system is filled with oxygen at a working pressure of about 0.1～1 Pa. MgF_2 window is used between the beamline and the system to separate different pressures, and spectral regions as well. MgF_2

window can transmit a wavelength longer than 113 nm[9]. The oxygen molecule bond energy is 498.36 kJ/mol[10] or about 240 nm (5.17 eV). This means a wavelength shorter than 240 nm can break the oxygen bond. So, after the MgF_2 window, only a photon energy between 113 ~ 240 nm is needed.

The whole experimental device is baked to decrease the background pressures of residual gases. Quadrupole mass spectra is connected in the middle chamber as shown in Fig. 2. Sample chamber is filled with pure oxygen with a purity is 99.999%. The pressure of sample chamber is set at 1.0, 1.2, 1.4, 1.6 Pa respectively. At each oxygen pressure, the mass spectrum is monitored with sample chamber set-up filled with oxygen only illuminated by SR and filled with oxygen. The oxygen species excited by SR were analyzed in both situations.

3 Experimented results

The molecule excited by high energy photons (113 ~ 240 nm) dissociates or ionizes as shown below[7]:

$$AB + h\nu(P) \rightarrow AB^+ + e \text{ or } AB',$$

$$AB' \rightarrow A + B.$$

The oxygen molecules illuminated by SR react as shown below[12]:

$$O_2 + h\nu \text{ (high energy photon)} \rightarrow 2O\cdot + \text{low energy photon},$$

$$O\cdot + O_2 + M \rightarrow O_3 + M + Q,$$

M is other molecule, Q is reaction heat.

Additional reaction is as follows:

$$O\cdot + O_3 \rightarrow 2O_2,$$

$$O_3 + e \rightarrow O_2 + O\cdot + e.$$

Only when the photon energy is higher than the molecule bond energy, a molecule can be dissociated or ionized. The oxygen molecule bond energy is 5.17 eV corresponds to a wavelength of 240 nm. The first ionization energy of oxygen is 1 310 kJ/mol. This means 13.618 eV is needed for oxygen ionization of atom. This ionization energy requires that the wavelength of incident photons is shorter than 91.2 nm, but after the MgF_2 window, the photon energy is lower than that, so the ionized species of oxygen monitored by mass spectra are few in the experimental process.

According to the oxygen dissociation reaction, the fractions are mainly oxygen atom and ozone, their relative mass numbers are 16 and 48, so the research is focused on these two. Fig. 3 and Fig. 4 show the background pressures of relative mass number 16 and 48 respectively. The average background pressure of relative mass number 16 is 3.33×10^{-7} Pa, and the average background mass number 48 is 3.33×10^{-8} Pa. Fig. 5 shows the curves of oxygen atom and ion pressures with SR incidence subtracting pressures without SR incidence when chamber oxygen gas pressure is set at 1.0, 1.2, 1.4, 1.6 Pa respectively. Fig. 6 shows the curves of ozone pressure with SR incidence subtracting pressure

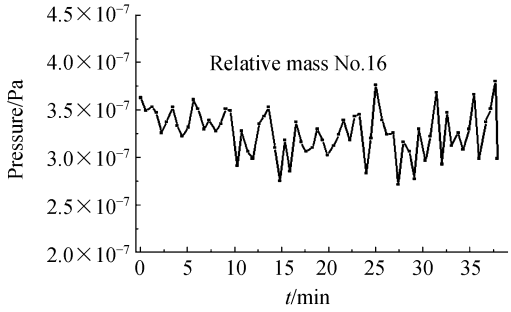

Fig. 3　Background pressure of relative mass No. 16

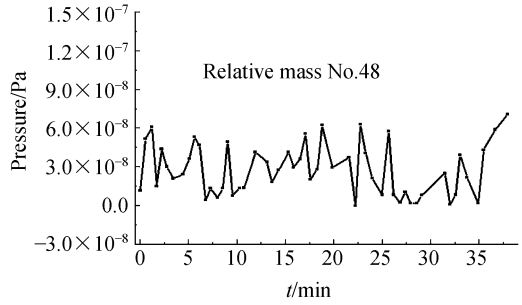

Fig. 4　Background pressure of relative mass No. 48

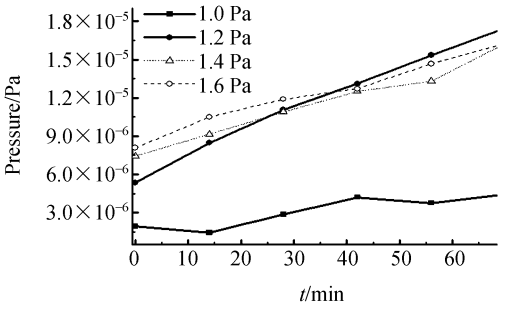

Fig. 5 Pressure curves of relative mass No. 16 with SR incidence subtracting pressure without SR at oxygen gas pressure of 1.0, 1.2, 1.4, 1.6 Pa.

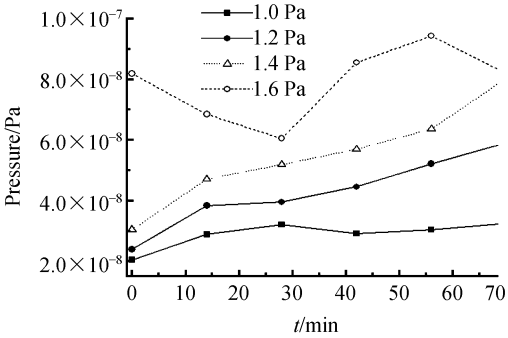

Fig. 6 Pressure curves of relative mass No. 48 with SR incidence subtracting pressure without SR at oxygen gas pressure of 1.0, 1.2, 1.4, 1.6 Pa.

without SR incidence when chamber oxygen gas pressure is different in the experiment, first of all the pressures of relative molecule mass numbers 16 and 48 are measured by quadrupole mass spectra when only pure oxygen gas is imported into the chamber ; then these two pressures were measured again with pure oxygen gas filled and SR incidence. Data are collected every 14 min and averages are calculated. Fig. 5 and Fig. 6 show that oxygen molecules can be dissociated by SR light to produce oxygen atom or ion and ozone, and their amounts are proportional to the illumination time of light under the same pressure. There may be a small difference in curves when the pressure is set at 1.2, 1.4, 1.6 Pa respectively because the species resulting from dissociation of oxygen have reached balance.

4 Conclusions

Oxygen molecules can be dissociated by SR light when the incident photon energy is higher than its bond energy to produce some oxygen species with strong oxidation, such as oxygen atom, oxygen ion and ozone. The amount of the oxygen species produced is proportional to the gas pressure of oxygen filled and the illumination time of synchrotron radiation light. These oxygen species can react with carbon contamination on optical element surface. The experimental results also show that the portion pressure of relative mass number 16 is about 1% of total pressure and the pressure of relative mass number 48 is about 0.005%～0.01% of total pressure in the cleaning process.

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Authors' biography: ZHONG Peng-pei received his Bachelor degree from the University of Science and Technology of China in 2005, and he is now a postgraduate student in Department of Precision Machinery and precision Instrumentation, University of Science and Technology of China.

ZHOU Hong-jun received her BS from University of Northeastern China in 1985, MS from the University of Centre England (UK) in 1999, Ph D from University of Science and Technology of China in 2006. Her current research interests include XUV spectral metrology, micro-fabrication and UHV vacuum system design. E-mail: hjzhou@ustc.edu.cn