

Laser irradiation effect on the damage of lubricant films

Rong Ji, Zhenxiang Xing, Yansheng Ma, Ji Feng Ying, Rongyan Zheng, Huiqing Xie, Xiaobai Wang, Angeline Yan Xuan Tan, Ching Mui Cho, and Jianwei Xu

Citation: *Journal of Vacuum Science & Technology B* **34**, 03H136 (2016); doi: 10.1116/1.4945821

View online: <http://dx.doi.org/10.1116/1.4945821>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvstb/34/3?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

[In situ measurement of the bonded film thickness of Z-Tetraol lubricant on magnetic recording media](#)

J. Appl. Phys. **108**, 084907 (2010); 10.1063/1.3500321

[Lubricant dynamics on a slider: "The waterfall effect"](#)

J. Appl. Phys. **105**, 074313 (2009); 10.1063/1.3104764

[Effect of N₂ annealing on AlZrO oxide](#)

J. Vac. Sci. Technol. A **21**, 1482 (2003); 10.1116/1.1586276

[Plasma polymerization and deposition of linear, cyclic and aromatic fluorocarbons on \(100\)-oriented single crystal silicon substrates](#)

J. Vac. Sci. Technol. A **20**, 1955 (2002); 10.1116/1.1513640

[Thermally induced Zr incorporation into Si from zirconium silicate thin films](#)

Appl. Phys. Lett. **79**, 2958 (2001); 10.1063/1.1415418



Instruments for Advanced Science

<p>Contact Hiden Analytical for further details: W www.HidenAnalytical.com E info@hiden.co.uk</p> <p>CLICK TO VIEW our product catalogue</p>	 <p>Gas Analysis</p> <ul style="list-style-type: none"> › dynamic measurement of reaction gas streams › catalysis and thermal analysis › molecular beam studies › dissolved species probes › fermentation, environmental and ecological studies 	 <p>Surface Science</p> <ul style="list-style-type: none"> › UHV TPD › SIMS › end point detection in ion beam etch › elemental imaging - surface mapping 	 <p>Plasma Diagnostics</p> <ul style="list-style-type: none"> › plasma source characterization › etch and deposition process reaction › kinetic studies › analysis of neutral and radical species 	 <p>Vacuum Analysis</p> <ul style="list-style-type: none"> › partial pressure measurement and control of process gases › reactive sputter process control › vacuum diagnostics › vacuum coating process monitoring
---	--	--	--	--

Laser irradiation effect on the damage of lubricant films

Rong Ji,^{a)} Zhenxiang Xing, Yansheng Ma, Ji Feng Ying, Rongyan Zheng, and Huiqing Xie
*Data Storage Institute, Agency for Science, Technology and Research (A-STAR), 2 Fusionopolis Way,
#08-01 Innovis, Singapore 138634*

Xiaobai Wang, Angeline Yan Xuan Tan, Ching Mui Cho, and Jianwei Xu^{a)}
*Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A-STAR),
2 Fusionopolis Way, #08-01 Innovis, Singapore 138634*

(Received 15 November 2015; accepted 30 March 2016; published 15 April 2016)

In contrast to conventional hard disk drives that work in an ambient condition, Heat-Assisted Magnetic Recording (HAMR) technology works by applying a highly focused laser beam to heat hard disk media up to around 400 °C. Under the HAMR condition, relevant hard disk components, including lubricant film, need to be extremely thermally stable. This paper studied the HAMR laser effect on the damage of our synthesized lubricant film together with a commercial lubricant Z-Tetraol for comparison by using an x-ray photoelectron spectroscopy and a time of flight secondary ion mass spectroscopy. The results revealed that our lubricant showed better laser resistance and thermal stability than the commercial lubricant. © 2016 American Vacuum Society.
[<http://dx.doi.org/10.1116/1.4945821>]

I. INTRODUCTION

The traditional magnetic recording technology has reached bottleneck, and it becomes more and more difficult to further increase the recording density due to the superparamagnetism. It was, however, found that some highly stable magnetic compounds¹ such as FePt, FePd, CoPt, and MnAl are able to store single bits in an extremely small area without being limited by the superparamagnetic effect even when heated above their Curie temperature. This thus led to the application of heat-assisted magnetic recording (HAMR) technology in hard disk drives. As a promising approach to enable a large increase in the storage recording density of hard disk drives,² HAMR works by applying a highly focused laser beam to rapidly heat up the requested localized zone to above the Curie temperature. As it works at a temperature of more than 400 °C, it requires current hard disk components including the lubricant film to be thermally stable at such a high temperature.

A lubricant film on a hard disk surface plays an important role in keeping reliability of the hard disk drives by protecting the media from any contact impact when a hard disk slider flies over disk media in an ultralow flying height and ultrahigh flying speed during recording. The existing commercial lubricant perfluoropolyethers (PFPE), such as Z-type Fomblins Z-DOL, Z-Tetraol, and A20H, show excellent properties such as good lubricity, low vapor pressure, low evaporation rate, low surface energy, high thermal stability, and low chemical reactivity at ambient hard disk operating conditions. HAMR technology requires the lubricant to retain all essential properties at high temperature and particularly under near field laser irradiation in order to avoid any lubricant degradation and decomposition, which may lead to failure of the whole hard disk drive.^{3–7}

In consideration of the overall HAMR requirements, it is necessary to improve thermal stability as well as laser

resistance of the lubricant. Therefore, many types of novel lubricants have been purposely designed and synthesized^{8–14} in order to fulfill the prerequisites of the HAMR lubricant. For example, an usual PFPE lubricant with OH end-groups substituted by benzophenone^{8,9} enhanced photothermal stability. Another example showed that photic ionic liquids are able to effectively improve the thermal stability of the lubricant.^{10,11} Recently, several types of lubricants with molecular structures derived from structural modification of conventional PFPE lubricants have been patented.^{12,13}

In recent years, we have also been devoted to design and synthesis of PFPE substituted cyclotriphosphazene-based lubricants. These lubricants have shown potential to serve as the HAMR lubricant by improving their thermal stability and laser resistance without compromising their tribology performance.¹⁴ The lubricant IDL1 is with a cyclotriphosphazene core, which is covalently linked with PFPE flexible chains through phosphorous–oxygen bonds. Being different from the most usual PFPE chains, the PFPE chains in IDL1 possess longer repeating units of OCF₂CF₂CF₂ than OCF₂CF₂. It was found that the lubricant IDL1 has enhanced thermal stability, improved laser resistance, comparable mobility, and other good tribology properties when compared to commercial lubricants.¹⁵ This paper will be focused on the study of the effect of laser irradiation on the damage of lubricated films including IDL1 and commercial Z-Tetraol for comparison purpose by using a thermogravimetric analyzer, an optical surface analyzer (OSA), a XPS, and a TOF-SIMS.

II. EXPERIMENT

A. Molecular structure of the lubricant

Z-Tetraol is a commonly used PFPE lubricant with the number-average molecular weight of 2500 and its chemical structure is shown below. It is a PFPE copolymer with the repeating units of CF₂CF₂O and CF₂O ($m/n \sim 1$).

^{a)}Electronic addresses: Ji_Rong@dsi.a-star.edu.sg; jw-xu@imre.a-star.edu.sg

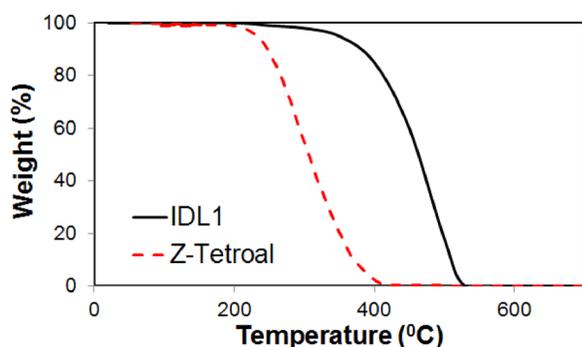
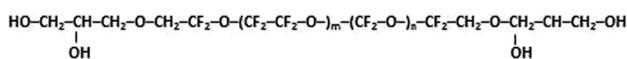
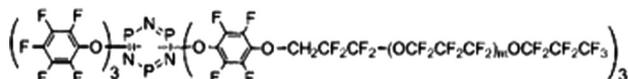


Fig. 1. (Color online) TGA diagrams of two lubricants Z-Tetraol and IDL1 in air.



The lubricant IDL1 with a molecular weight of 7900 was with a cyclotriphosphazene inorganic core, which is covalently incorporated into PFPE flexible chains with a repeating unit $\text{OCF}_2\text{CF}_2\text{CF}_2$. Its chemical structure is given below:



B. Experimental details

The thermal stability of two lubricants was first analyzed by TGA, which gives us the information on the stability of bulk samples. The TGA analysis was conducted on Perkin Elmer Pyris 1, the starting material is 30 mg, and the heating rate is $10^\circ\text{C}/\text{min}$ in air.

Thin film samples of the lubricant are used for laser irradiation and OSA, XPS, TOF-SIMS analyses. On a 2.5 in. glass disk, 1.2 nm of Z-Tetraol or IDL1 lubricant films were deposited on top of a 1 nm $\alpha\text{-C:N}$ over 4 nm $\alpha\text{-C:H}$ carbon overcoat on 2.5 in. HAMR magnetic disks. On a HAMR system that is developed by DSI,¹⁶ the disk was irradiated under a laser with a wavelength of 532 nm, a pulse width of 1.3 ns, an average/peak power of 19.07 mW/1.47 kW, and a spot size of around $260\ \mu\text{m}$. The samples with laser spot scans in the Y direction to 1 mm and both X and Y directions to a $1 \times 1\ \text{mm}$ area were prepared. The total laser heating time for each point in the area

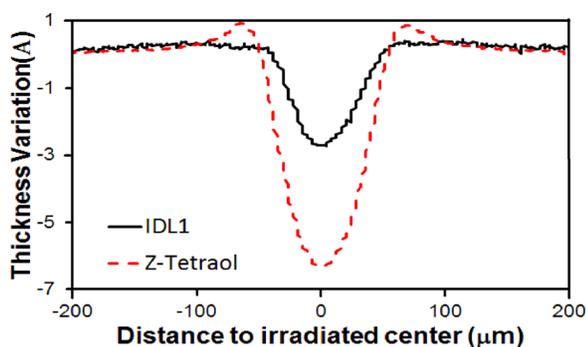


Fig. 2. (Color online) OSA line scan results of Z-Tetraol and IDL1 films after laser irradiation.

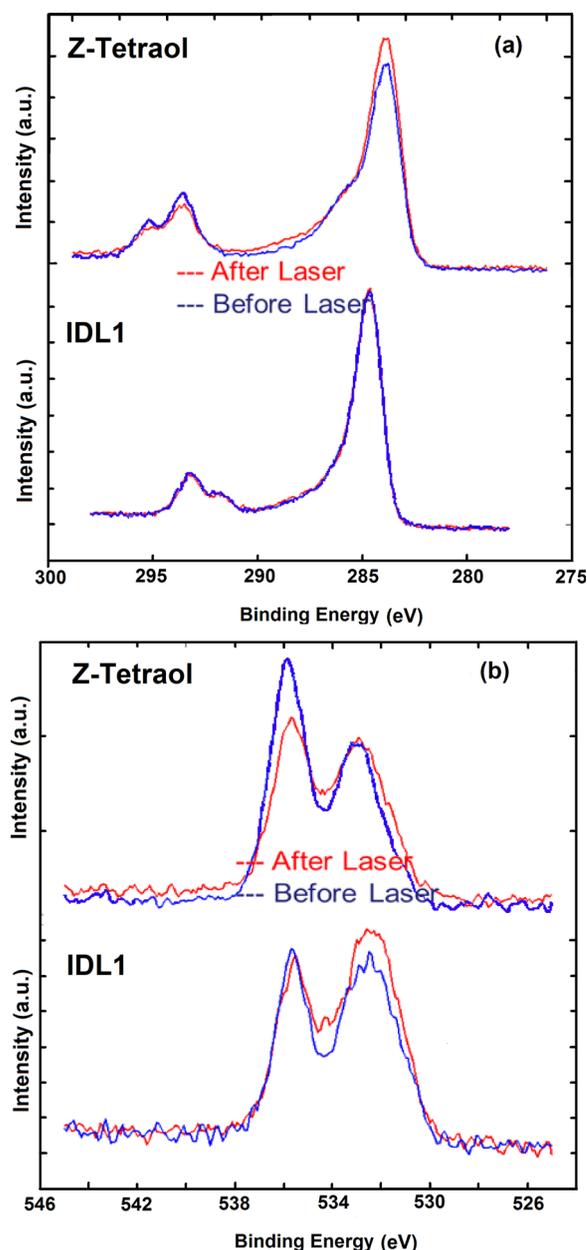


Fig. 3. (Color online) XPS spectra of (a) C1s and (b) O1s before and after laser irradiation for Z-Tetraol and IDL1 sample.

is 1 ms. After the laser irradiation, the surface topographical changes of the sample with laser spot scans in the Y direction to 1 mm were first examined using OSA. The compositional changes of the sample with laser spot scans in both X and Y directions to a $1 \times 1\ \text{mm}$ area were then analyzed using a XPS and TOF-SIMS. OSA Q-phase images were taken using Candela 7100. The XPS measurement was conducted on a PHI Quantera SXM scanning x-ray microprobe with a monochromatic $\text{Al K}\alpha$ source. The system was operated at 15 keV, 40 W, 45° take-off angle, 55 eV pass-energy with 0.1 eV energy gap, and $100\ \mu\text{m}$ size of beam. TOF-SIMS analysis was carried out on a PHI TRIFT II equipment using a 15 keV Ga^+ primary ion source for both etching and surface analysis. For surface ion mapping, the ion dose is less than 6×10^{12} ions/ cm^2 , and the analysis size was set as $100 \times 100\ \mu\text{m}$.

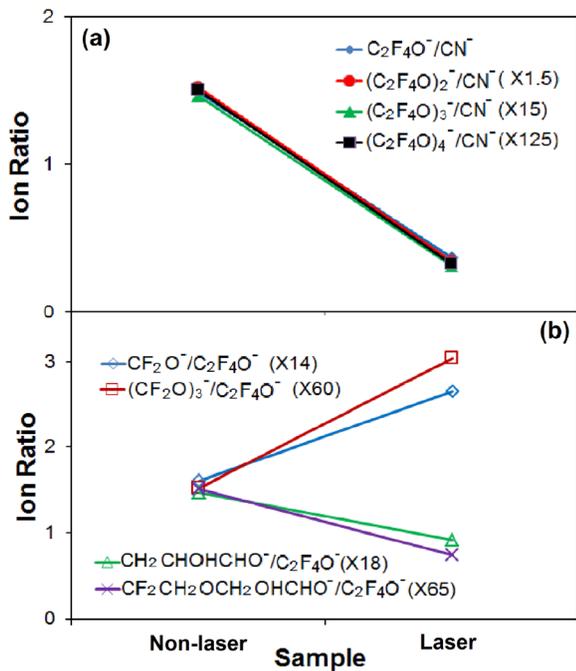


FIG. 4. (Color online) TOF-SIMS ion ratios of (a) $(C_2F_4O)_n^-/CN^-$, (b) $(CF_2O)_n^-/C_2F_4O^-$, and end-group/ $C_2F_4O^-$ for Z-Tetraol sample with and without laser irradiation.

III. RESULTS AND DISCUSSION

The thermal stability of lubricants Z-Tetraol and IDL1 were examined. The decomposition temperature, which is defined as the temperature at which 5% weight loss occurs, is used to evaluate the thermal stability of the bulk lubricant.

Figure 1 shows the TGA diagrams of both Z-Tetraol and IDL1 bulk lubricants. IDL1 clearly showed much higher decomposition temperature than Z-Tetraol. It was observed that Z-Tetraol and IDL1 have decomposition temperatures of 231 and 350 °C, respectively. The excellent thermal stability and low evaporation rate of IDL1 are most probably due to the relatively high molecular weight as well as its longer repeat unit $(OCF_2CF_2CF_2)$ of the perfluoropolyether chain than Z-Tetraol series.

OSA result of the laser irradiated zones is given in Fig. 2. After calibrating the lubricant thickness with XPS measurement, OSA results show that under same laser irradiation condition, IDL1 is with shallower depth than Z-Tetraol. This indicates that the IDL1 film has much better laser resistance than the Z-Tetraol film. As IDL1 has no noticeable adsorption in the laser wavelength range from 380 to 800 nm,^{14,15} it is believed that photo degradation can be ignored here, and the thickness variation of the IDL1 film is mainly because of the thermal effect. The shallow laser irradiation depth of IDL1 film coincides with its better thermal stability than that of Z-Tetraol film.

Figure 3 shows the XPS narrow scan of C1s and O1s peaks of both lubricant films before and after laser irradiation. In Fig. 3(a), the peaks at 284.8–289, 292, and 294 eV are assigned to C1s of C–C/C–O/C=O bonds, C–F₂ bond, and C–F₃ bond, respectively. The C1s signals of C–F₂ and C–F₃ bonds originate from the lubricant film, while the C1s signals of C–C/C–O/C=O bonds can come from both the lubricant film and the carbon overcoat, which is an immediate layer below the lubricant layer. Therefore, the decrease in C–F₂ and C–F₃ C1s signals and at the same

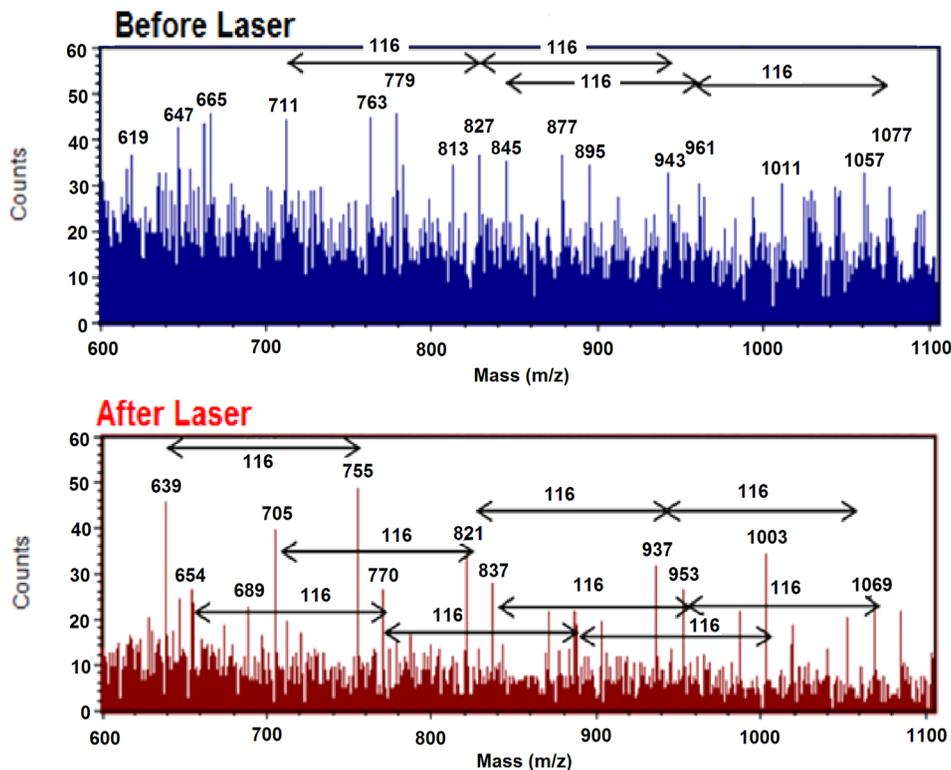


FIG. 5. (Color online) TOF-SIMS mass spectra of the Z-Tetraol lubricant film in the mass range of 600–1100 amu before and after laser irradiation.

time the increase in C–C/C–O/C=O C1s signals suggest the decreased signal from the lubricant film and the increased signal from the carbon overcoat. The results show that laser irradiation induces a larger loss in film thickness of the Z-Tetraol film than the IDL1 film, which is consistent with OSA results. In Fig. 3(b), the peak at ~ 531.5 – 533 eV are ascribed to the O1s of O–C and O=C bonds, and the peak at ~ 535.8 eV belongs to the O1s of the O–F_x bond. The obvious decrease in binding energy of the O1s of O–F_x peak for the Z-Tetraol lubricant film

and the limited change in the O1s of O–F_x peak for the IDL1 lubricant film after laser irradiation again support that the degree of changes in the lubricant's thickness is consistent with the thermal stability. Furthermore, the signal broadening of the O1s of O–C and O=C bonds for the Z-Tetraol lubricant film and the increased intensity of the O1s of O–C and O=C bonds for the IDL1 film after laser irradiation is likely to suggest certain information on lubricant decomposition, which will be analyzed by TOF-SIMS.

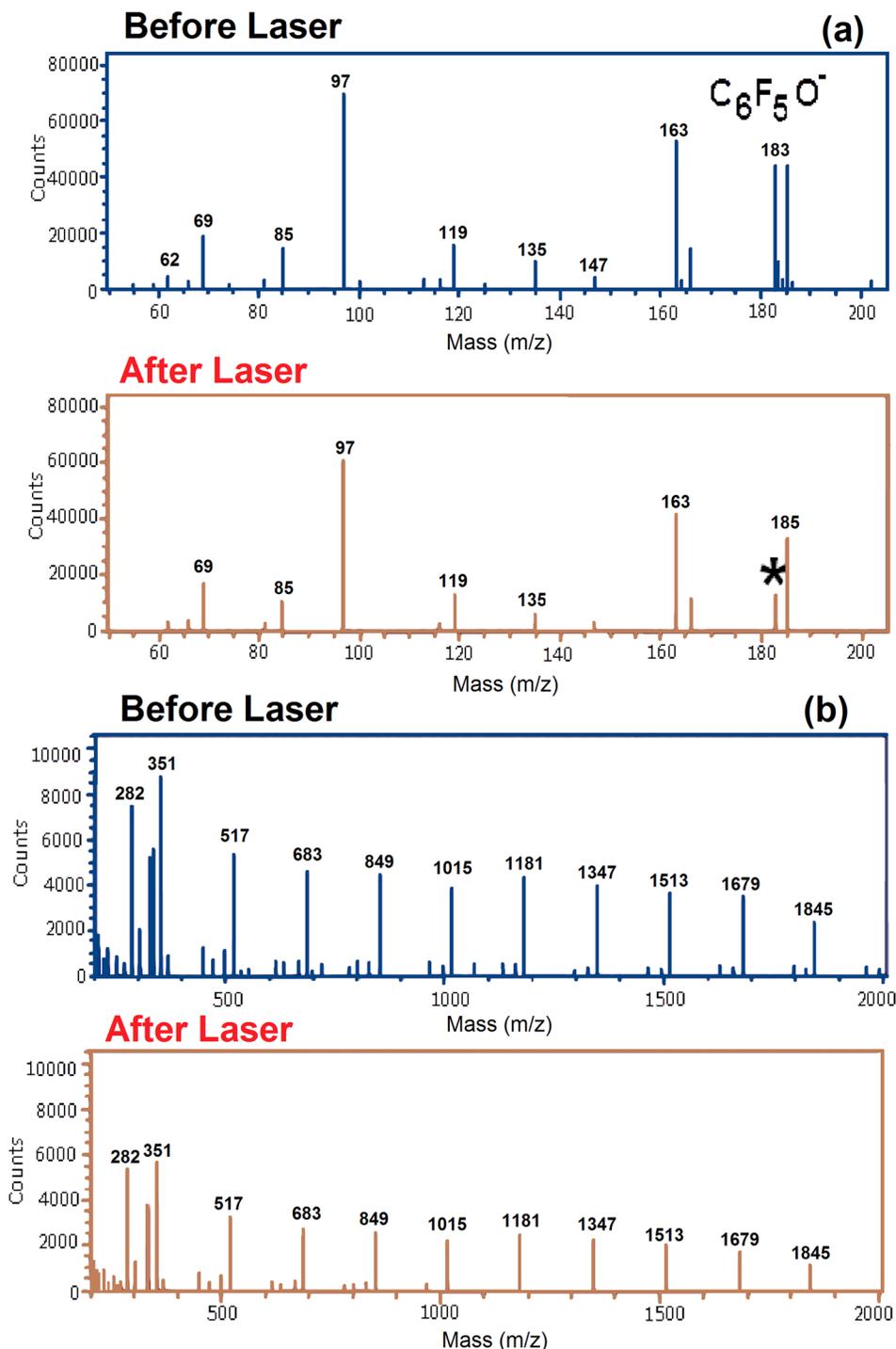


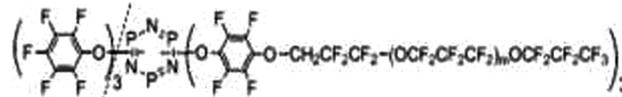
Fig. 6. (Color online) TOF-SIMS spectra before and after laser irradiation of IDL1 film in the mass range of (a) 50–205 amu and (b) 250–2000 amu.

TOF-SIMS analysis of the Z-Tetraol film is shown in Fig. 4. The laser effect on the damage of the Z-Tetraol lubricant film is studied through the analysis of the ratio changes of its different ion fragments. Z-Tetraol's molecular structure could be grouped as three segments: $(C_2F_4O)_m$, $(CF_2O)_n$, and end-group $CF_2CH_2OCH_2OHCH_2OH$. The ion ratios of $(C_2F_4O)_m^-/CN^-$ are given in Fig. 4(a). After laser irradiation, all $(C_2F_4O)_m^-/CN^-$ ratios drop in comparison with reference. It was reported that TOF-SIMS ion ratio of PFPE backbone over nitrogenated carbon ion fragment of CN^- can be used as a lubricant thickness indicator.¹⁷ Our results showed that laser irradiation made the lubricant layer thinner. All signals could be normalized to C_2F_4O . Figure 4(b) shows $CF_2O^-/C_2F_4O^-$, $(CF_2O)_3^-/C_2F_4O^-$, $C_3H_5O_2^-/C_2F_4O^-$, and $CF_2OC_3H_5O_2^-/C_2F_4O^-$ ratios for reference and laser irradiated location, clearly showing that the ratio of $(CF_2O)_n/C_2F_4O$ increases and the $C_3H_5O_2^-/C_2F_4O^-$ and $CF_2OC_3H_5O_2^-/C_2F_4O^-$ ratios decrease from reference to laser irradiated location. This reveals that the lubricant decomposes upon laser irradiation, the decomposition happens more significant at the end-group of the lubricant, and the final material is with higher amount of perfluoropoly-methylene oxide component.

Figure 5 shows the ion mass spectra of the lubricant Z-Tetraol sample in the mass range of 600–1100 amu before and after laser irradiation. It is observed that the characteristic ion fragments of $HOCH_2CHOHCH_2OCH_2CF_2O(C_2F_4O)_m(CF_2O)_nCF_2CH_2OCH_2^+$ at 711, 827, 943, 845, 961, and 1077 amu becomes not obvious after laser irradiation. On the other hand, the characteristic ion fragments of $OCFO(C_2F_4O)_m(CF_2O)_nCF_2OH^+$ at 639, 705, 755, 654, 770, 821, 886, 937, 953, and 1069 amu become significant after laser irradiation. This also again confirms that laser irradiation induces Z-Tetraol lubricant decomposition and indicates that the laser irradiation induces Z-Tetraol lubricant decomposition from original molecule to more $O=CFO(C_2F_4O)_m(CF_2O)_nCF_2=O$ component.

Similar experiment was performed on the IDL1 lubricant film, and TOF-SIMS spectra before and after laser irradiation of the IDL1 film in the mass range of (a) 50–205 amu and (b) 250–2000 amu are shown in Fig. 6. Except that the intensity of the overall spectrum fingerprint decreases, the lubricant's thickness decreases as evidenced by the obvious decrease in the intensity of ion fragment of $C_6F_5O^-$ (183 amu) after laser irradiation. This might indicate that laser irradiation breakdowns phosphorous–oxygen bond bridging between the side-chain and the cyclotriphosphazene core in IDL1 as shown

below. The cleavage of the phosphorous–oxygen bond which joins flexible PFPE leads to increase in O1s signals from O–C and O=C components.



IV. SUMMARY AND CONCLUSIONS

This paper studied the laser induced damage on commercial and our synthesized lubricant films. It was found that HAMR laser irradiation caused decomposition of both end-group and backbone components of the Z-Tetraol lubricant. In contrast, IDL1 showed better thermal stability; however, the cleavage of phosphorous–oxygen bond bridging the flexible PFPE and the cyclotriphosphazene core was observed. This would give us insight into how to design and synthesize new types of cyclotriphosphazene-based lubricants. For example, the introduction of more thermally stable moieties in the lubricant molecule to further enhance the thermal stability and laser resistance of lubricant film has yet to be demonstrated.

¹D. Weller and A. Moser, *IEEE Trans. Magn.* **35**, 4423 (1999).

²R. E. Rottmayer *et al.*, *IEEE Trans. Magn.* **42**, 2417 (2006).

³P. H. Kasai, *Macromolecules* **25**, 6791 (1992).

⁴C. M. Mate, P. H. Kasai, and G. W. Tyndall, *IEEE Trans. Magn.* **34**, 1744 (1998).

⁵P. H. Kasai and A. M. Spool, *IEEE Trans. Magn.* **37**, 929 (2001).

⁶P. H. Kasai and V. Raman, *Tribol. Lett.* **15**, 15 (2003).

⁷P. H. Kasai and A. Wakabayashi, *Tribol. Lett.* **31**, 25 (2008).

⁸J. Lee, S. W. Chun, H. J. Kang, and F. E. Talke, *Tribol. Lett.* **28**, 117 (2007).

⁹M. Gauvin, H. Zheng, B. Suen, J. Lee, H. J. Kang, and F. E. Talke, *IEEE Trans. Magn.* **47**, 1849 (2011).

¹⁰H. Kondo, K. Hatsuda, N. Tano, M. Ito, K. Yun, and M. Watanabe, *IEEE Trans. Magn.* **50**, 3302504 (2014).

¹¹H. Kondo, K. Hatsuda, N. Tano, M. Ito, K. Yun, and M. Watanabe, U.S. patent 20150353558 (27 December 2013).

¹²B. E. Knigge and M. M. Biswas, U.S. patent 20140234666 (19 February 2013).

¹³L. Li, M. J. Stirniman, and J. P. Yang, U.S. patent 20120219826 (28 February 2011).

¹⁴J. W. Xu, R. Ji, X. B. Wang, A. Y. X. Tan, C. M. Cho, C. B. He, R. Ji, H. Q. Xie, and J. W. H. Tsai, U.S. patent 20150184104A1 (2 July 2015).

¹⁵X. B. Wang, A. Y. X. Tan, C. M. Cho, Q. Ye, C. B. He, R. Ji, H. Q. Xie, J. W. H. Tsai, and J. W. Xu, *Tribol. Int.* **90**, 257 (2015).

¹⁶Y. Ma, L. Gonzaga, C. An, and B. Liu, *IEEE Trans. Magn.* **47**, 3445 (2011).

¹⁷B. C. Zhang, H. K. Liu, and S. Chang, *Appl. Surf. Sci.* **231–232**, 336 (2004).