TIME-RESOLVED QUADRUPOLE MASS SPECTROMETRIC STUDIES ON PULSED LASER ABLATION OF TiO₂

YONGXIN TANG, ZHENHUI HAN and QIZONG QIN*

Laser Chemistry Institute, Fudan University, Shanghai 200433, P. R. China

(Received 8 February 1999; In final form 19 February 1999)

Pulsed laser ablation of TiO₂ at 355 nm and 532 nm has been investigated using an angle- and time-resolved quadrupole mass spectrometric technique. The major ablated species include O (m/e = 16), O₂ (m/e = 32), Ti (m/e = 48), TiO (m/e = 64) and TiO₂ (m/e = 80). The time-of-flight (TOF) spectra of ablated species are measured for the ionic and neutral ablated species, and they can be fitted by a Maxwell–Boltzmann (M–B) distribution with a center-of-mass velocity. The measured angular distributions of the ionic species (O⁺ and Ti⁺) and the neutral species (O and Ti) can be fitted with \( \cos^n \theta \) and \( a \cos \theta + (1 - a) \cos^n \theta \), respectively. In addition, a continuous wave oxygen molecular beam is introduced into the ablated plume, and the enhancement of the signal intensities of TiO is observed. It implies that the ablated Ti atoms/ions species can react with ambient oxygen molecules in the gas phase. In the meanwhile, the physicochemical mechanism of pulsed laser ablation of TiO₂ is discussed.

Keywords: Quadrupole mass spectrometry; laser ablation; TiO₂; time-of-flight

Thin films of titanium dioxide (TiO₂) have been widely proposed for various applications in optics, microelectronics, chemistry, environmental science and catalysis because of their physical stability, high refractive index, excellent transmittance in the visible and near-infrared region, and the ability to decompose H₂O and degrade organisms [1–6]. TiO₂ thin films have been grown with a number of techniques, such as sol-gel process, chemical vapor deposition, electron beam evaporation, ion assisted deposition and sputtering, as well as pulsed

*Corresponding author. Tel.: +86 21 65102777, Fax: +86 21 65102777, e-mail: qzqin@srcap.sth.sh.cn

99
laser deposition (PLD). Among these techniques, PLD provides a convenient method for fabricating TiO$_2$ thin films because of its low-temperature process, capability for reactive deposition and ability to transfer nearly the original stoichiometry of a bulk target to the deposited film. Akimor et al. [7] reported the first fabricating of TiO$_2$ thin film using PLD method. After then, many groups have utilized various PLD techniques to deposit TiO$_2$ thin films [2, 3, 8, 9]. Recently, TiO$_2$ films were fabricated by laser reactive deposition in an O$_3$/O$_2$ ambient with a metallic Ti target in our laboratory [10]. However, previous papers rarely focused on the understanding of the laser ablated plume and the nature of the laser ablation process, which needs to be studied further.

In this paper, we try to identify the ionic and neutral species ablated from TiO$_2$ as well as to determine their translational energies and spatial distributions using an angle- and time-resolved quadrupole mass spectrometric method. In addition, a continuous wave (cw) O$_2$ molecular beam was used and introduced into the ablated plume to examine the reactions of ablated species with O$_2$ in the gas phase. We hope to obtain more information on the possible physicochemical mechanism of the laser ablation of TiO$_2$.

1. EXPERIMENTAL

The experimental apparatus has been reported previously [11]. Briefly, there was a rotatable sample target on which a TiO$_2$ pellet was mounted at the center of the chamber, and this chamber can be pumped down to a base pressure of $\sim 10^{-6}$ Torr. TiO$_2$ pellet was prepared by uniaxially compressing TiO$_2$ powder (99.95%). The 355 nm and 532 nm laser beams were generated by the third- and second-harmonic frequencies of a Q-switched Nd: YAG laser (Spectra-Physics, GCR-190), and were focused and irradiated onto the target surface with an incident angle of 45° to the surface normal. The laser was operated with a pulse width of 8 ns and a repetition rate of 10 Hz. The diameter of the laser spot was around 1 mm.

A rotatable quadrupole mass spectrometer (QMS; ULVAC MSQ-400) was employed to measured the mass and angular distributions of the ablated species. The flight distance of the ablated species from the
target surface to the ionizer of the QMS was 18 cm. Their TOF spectra were recorded by a 10 MHz transient recorder, which was interfaced to a PC computer and triggered synchronously by the laser pulse. Only ionic species were detected with the ionizer of the QMS switched off, and the overall ions generated both from the direct TiO₂ ablation as well as the fragments of neutral ablated species from a 70 eV electron impact ionization were detected with the ionizer switched on. The average translational energies of the ablated species were obtained with a calibration of the ion drift time \( t_d \) in the quadrupole mass spectrometer.

In general, the measured TOF spectrum can be fitted by a Maxwell–Boltzmann (M–B) distribution with a center-of-mass velocity:

\[
F(t) = A t^{-4} \exp(-b_1 t^{-2} + b_2 t^{-1})
\]  

where \( A, b_1 \) and \( b_2 \) are the simulation parameters \( b_1 = mL^2/2kT_s \) and \( b_2 = 2b_1u/L \), \( t \) is the flight time, \( u \) is the center-of-mass velocity, \( L \) is the flight distance, \( m \) is the mass of the ablated species, \( k \) is the Boltzmann constant and \( T_s \) is a temperature parameter. When the detected ion originates from two or more parent components, the TOF spectrum for the detected ion can be simulated by a multi-component shifted M–B distribution:

\[
F(t) = \sum_{i=1}^{p} F_i(t) = \sum_{i=1}^{p} c_i t^{-4} \exp(-b_{1i} t^{-2} + b_{2i} t^{-1})
\]

where \( p \) is the number of components, \( c_i, b_{1i} \) and \( b_{2i} \) are the simulation parameters of the component whose order number is \( i \). The center-of-mass velocity of each component can be obtained from these simulation parameters [12].

A cw supersonic oxygen molecular beam was generated by an adiabatic expansion of O₂ through a 0.1 mm diam nozzle into vacuum. A three-stage differentially pumped system was used to maintain a base pressure of \( \sim 5 \times 10^{-5} \) Torr in the reaction chamber. A collimated O₂ beam provided by a supersonic nozzle-skimmer arrangement was introduced to skim the sample surface for examining the interaction of ablated species with ambient oxygen.
2. RESULTS AND DISCUSSION

2.1. Mass Distributions of Ablated Species

The time-of-flight (TOF) spectra of the species ejected from the laser ablation of a TiO$_2$ target with mass to charge (m/e) 16(O), 32(O$_2$), 48(Ti), 64(TiO) and 80(TiO$_2$) have been measured, and the mass distributions of the ablated species are obtained by time-integrating their TOF signals. Figure 1(a) presents the mass distribution of ablated species when the laser fluence is fixed to be 500 mJ/cm$^2$ at 355 nm. It is seen that the relative intensities of the O and Ti are dominant, O$_2$, TiO and TiO$_2$ are of comparable intensities, while Ti dimer and TiO$_n$ (n > 2), whether the ionic or the neutral species, are not observed. Figure 1(b) presents the mass spectrum of ablated species measured at 532 nm. Comparison with Figure 1(a), it is evident that the mass distributions of the ablated species obtained by using different laser wavelength at 532 nm and 355 nm are nearly the same, except that 355 nm radiation tends to generated more ionic Ti$^+$ species.

2.2. Simulation of the TOF Spectra

The TOF spectra of the ablated species can usually be fitted using a shifted M–B distribution with a center-of-mass velocity. As an example, we examine the simulations of TOF spectra of TiO$^+$ and Ti$^+$ measured at 532 nm with the ionizer switched on and they are shown in Figures 2(a) and (b), respectively. It can be found that the TOF spectrum of TiO$^+$ can be well fitted with a three-component shifted M–B distribution i.e., the Eq. (2) with $p = 3$. The first fast peak originates from the nascent ionic TiO$^+$, while the other broader peak of TiO$^+$ should be attributed to the neutral TiO and TiO$_2$, and the two fitted components correspond to the TiO$^+$ ions generated from 70 eV electron-impact ionization of TiO and TiO$_2$ in the ionizer of QMS. Similarly, the TOF spectrum of Ti$^+$ in Figure 2(b) can be fitted with a four-component shifted M–B distribution i.e., the Eq. (2) with $p = 4$, and the four components are attributed to nascent Ti$^+$ ions as well as the neutral Ti, TiO and TiO$_2$, respectively.

By fitting the TOF spectra of the ablated species measured at 532 nm, we estimated the most probably velocity $v_p$, the center-of-mass
velocity $u$, the average kinetic energy $E_T$, and Mach number $M$. The simulation results are listed in Table I. It is seen that all of the neutral Ti-containing species Ti, TiO and TiO$_2$ have the velocities in the range $5 \times 10^2$ to $9 \times 10^2$ m/s, which corresponding to the kinetic energy from 0.2 to 0.4 eV. Note that these neutral species have no center-of-mass
FIGURE 2. TOF spectra of TiO$^+$ (a) and Ti$^+$ (b) measured by QMS with ionizer filament on at 532 nm. The dashed lines are the fits to a three- or four-component shifted M – B distribution.

velocity ($u = 0$). For the ablated ionic species, however, their most probably velocities and kinetic energies are much higher than those of the neutral species. Moreover, their TOF spectra should be simulated
TABLE I  The simulation results of ablated species from TiO₂ at 532 nm

| Species | m/e | \( \nu_p \) (10³ m/s) | \( u \) (10³ m/s) | Mach number | \( E_T \) (eV) |
|---------|-----|------------------------|-----------------|-------------|--------------|
| Ti      | 48  | 0.92                   | 0               | /           | 0.43         |
| TiO     | 64  | 0.80                   | 0               | /           | 0.42         |
| TiO₂    | 80  | 0.51                   | 0               | /           | 0.22         |
| Ti⁺     | 48  | 3.35                   | 2.4             | 1.13        | 5.6          |
| TiO⁺    | 64  | 4.11                   | 1.0             | 0.25        | 11.2         |

by a shifted M–B distribution, and the center-of-mass velocity is estimated to be \( 2.4 \times 10^3 \) and \( 1.0 \times 10^3 \) m/s for Ti⁺ and TiO⁺, respectively. These simulation results imply that the different mechanism should be proposed to explain the generation of the ionic and neutral ablated species in the laser ablation of TiO₂. It is well known that the ablated ionic species generated by a non-thermal process possess high kinetic energy and a center-of-mass velocity via an electronic excitation or laser-plume interaction [13]. So the nascent ionic species, such as Ti⁺ and TiO⁺, ablated from the TiO₂ target mostly originate from non-thermal photodissociation and photoionization processes. Since the neutral ablated Ti-containing species are well fitted by an M–B distribution with low kinetic energies and \( u = 0 \), it is reasonable to assume that the neutrals come from a thermal process such as physical evaporation from the target surface with laser-induced thermal heating.

2.3. Angular Distributions of Ablated Species

Angular distribution of laser ablated species plays an important role in the pulsed laser deposition of the thin films as well as in the examination of the underlying mechanism of laser ablation. According to the viewpoint we describe in Ref. [14], the angular distribution of the ablated species mainly depends on the mechanism of laser ablation. For a thermal evaporation process, the ejection of the ablated species is moderately forward directed as a cosine distribution or Knudsen law. For a non-thermal process, however, the ablated species in the laser induced plasma undergo a secondary ejection along the surface normal and create a high forward-peaked expansion, and the angular distribution of the ablated species can be described by a \( \cos^n \theta \) function, where \( n \) is called sharpness parameter. In addition, in some
ablation processes, both thermal and non-thermal processes are important, and a bicosine function $a \cos \theta + (1 - a) \cos^n \theta$ can be well used to simulate the angular distribution of the ablated species, in which the former term $a \cos \theta$ respects a thermal evaporation process and the later term $(1 - a) \cos^n \theta$ corresponds to a non-thermal process. Figure 3 shows the measured angular distributions of $O^+$, O, Ti$^+$, Ti$^+$/Ti$^+$. 

FIGURE 3  The angular distributions of the ablated species Ti$^+$, Ti, O$^+$ and O at 355 m.
LASER ABLATION OF TiO$_2$ and Ti ablated from a TiO$_2$ target. It can be seen that the angular distribution of Ti$^+$ ions detected with the ionizer switched off is very sharp and can be fitted by $\cos^n \theta$ ($n \approx 6$). For the atomic Ti detected with the ionizer switched on, however, the angular distribution is broader, and should be fitted using a bicosine function $a \cos \theta + (1 - a) \cos^n \theta$ with $n \approx 22$ and $a \approx 0.79$. Additionally, the ablated O$^+$ and O can also be well fitted using the functions of $\cos^n \theta$ ($n \approx 10$) and $a \cos \theta + (1 - a) \cos^n \theta$ ($n \approx 9$ and $a \approx 0.4$), respectively. The angular distributions of the ablated species, whether neutral or ionic, all diviate from Knudsen law, which suggests that the laser ablation of TiO$_2$ is not a simple laser-induced thermal evaporation process. Thus our results imply that both the neutral Ti and O atoms originate from a thermal evaporation and a non-thermal ejection process, while the nascent ions of Ti$^+$ and O$^+$ are only generated from a non-thermal process as their angular distributions are well fitted by a $\cos^n \theta$ function.

### 2.4. Laser Ablation of TiO$_2$ with an O$_2$ Molecular Beam

In the laser deposition of thin films, oxygen or oxygen-containing gas is always used as a reactive ambient gas. So the characteristics of laser ablation are also connected to the interaction of the ablated species with a reactive ambient gas. In order to examine whether ambient O$_2$ molecules react directly with the ablated Ti-containing species, an O$_2$ molecular beam was introduced into the ablation plume and the TOF spectra of the ablated species were measured simultaneously. Figure 4 shows the effect of the presence of oxygen on the time-of-flight signals of the ablated species. It can be found in Figure 4(a) that the signal intensity of TiO$^+$ measured at the introduction of an O$_2$ beam is higher than that measured in vacuum, while the profiles of two signals are approximately the same. As shown in Figure 4(b), however, the TOF signal intensity of Ti$^+$ measured in an O$_2$ beam condition is found to be lower than that in vacuum, which is contrary to that for TiO$^+$ signal. These results suggest that the ablated TiO$^+$ species originate not only from the laser ablation of the TiO$_2$ target directly, but also from the reactions of ablated Ti atoms/ions with introducing O$_2$ molecules. Furthermore, these reactions lead to the
expense of Ti atoms/ions which results in decreasing of the TOF signal intensity. Additionally, the peak positions and signal profiles for the TOF signals in Figures 4(a) and (b) show no obvious changes under the introduction of an $O_2$ beam or not, it may be due to the fact that the kinetic energies of the ablated species are much higher, and it can not be disturbed by the reactions of ablated Ti species with $O_2$ molecules.
3. CONCLUSION

An angle- and time-resolved quadrupole mass spectrometric method was successfully used to investigate the mass, velocity, and angular distributions of ionic and neutral species generated from the laser ablation of TiO$_2$ at 532 nm and 355 nm. The velocity and angular distributions for neutral and ionic species show that the generation of the nascent ion species might be achieved by non-thermal photochemical and photoionization processes, while both thermal and non-thermal processes play an important role for the generation of neutral ablated species. The introduction of an oxygen molecules beam experiment gives one direct evidence for the interaction of ablated Ti ions/atoms with oxygen molecules. Apparently, the TiO$_2$ laser ablation mechanism is complicated and the details of the ablation processes will be further investigated.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (grant No. 29683001).

References

[1] Watanabe, Shigeyuki and Nozoye, Hisakuzu (1998). *Appl. Surf. Sci.*, 130–132, 822.
[2] Garapon, C., Champeaux, C., Mugnier, J., Panczer, G., Mareget, P., Catherinot, A. and Jacquier, B. (1996). *Appl. Surf. Sci.*, 96–98, 836.
[3] Dai, C. M., Su, C. S. and Chun, D. S. (1991). *J. Appl. Phys.*, 69, 3766.
[4] Stashans, Arvids, Lunell, Sten, Bergstrom, Robert, Hagfeldt, Anders and Lindquist, Sten-Eric (1996). *Physical Review B*, 53, 159.
[5] Hugenschmidt, M. B. and Gamble, L. (1994). *Surf. Sci.*, 302, 329.
[6] Kavan, L. and Gratzal, M. (1995). *Electrochimica Acta*, 40, 643.
[7] Akimor, A. G., Gagarin, A. P. and Dagurov, V. G. (1980). *Sov. Phys. Tech. Phys.*, 25, 1439.
[8] Durand, H. A., Brimaud, J. H., Hellman, O., Shibata, H., Makita, Y., Gesbert, D. and Meyrueis, P. (1995). *Appl. Surf. Sci.*, 86, 122.
[9] Snakur, H. O. and Guning, W. (1989). *Appl. Opt.*, 26, 2806.
[10] Zhengwen, Fu, Mingfei, Zhou, Shengkun, Zhang, Liangyao, Chen and Qizong, Qin (1998). *Chinese Science Bulletin*, 43, 1344.
[11] Qin, Qizong, Zhou, Mingfei and Mao, Dunmin (1997). *Appl. Surf. Sci.*, 119, 321.
[12] Zheng, J. P., Huang, Z. Q., Shaw, D. T. and Kwok, H. S. (1989). *Appl. Phys. Lett.*, 54, 280.
[13] Kwok, H. S. (1992). *Thin Solid Films*, 218, 277.
[14] Dang, H. J., Han, Z. H., Dai, Z. G. and Qin, Q. Z. (1998). *International J. Mass Spectrometry*, 178, 205.