Photoelectrons Ejected from a Zirconium Surface by One-Photon or Two-Photon Laser Ionization in Air

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Photoelectrons Ejected from a Zirconium Surface by One-Photon or Two-Photon Laser Ionization in Air

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In order to study interactions between photons and a metal surface, a new laser photoionization apparatus was constructed and applied to photoionization of a Zr surface by one-photon or two-photon laser ionization in air. The time profile of photocurrents consisted of two components. One short component was attributed to photoelectrons from the Zr surface and the other long one was explained as due to \( \text{O}_2^- \) anions formed by an electron attachment to \( \text{O}_2 \). The dependence of the peak voltage and the recovery time on the applied voltage between the Zr rod and a charged particle collector was measured.

Introduction

Interactions between photons and a solid surface are of significant importance in understanding the formation processes of advanced materials by laser irradiation.\(^1\) We have recently initiated studies on interactions between photons and a solid surface using a Nd:YAG laser. Here, preliminary results for photoelectric effects on a Zr surface in air are communicated.

Experimental

Figure 1 shows the laser-photoionization apparatus used in this study. It consists of a Nd:YAG laser (Continuum SL I-10), a Zr rod, a nickel mesh, a high voltage supply (Kawaguchi Electronic Works V-703), a current amplifier (Keithley 428), and a digital oscilloscope (Lecroy 9360S). The wavelengths of the Nd:YAG laser used in this study were 266 and 532 nm. The pulse width was 4-6 ns and the repetition rate was 10 Hz. The laser pulse energy was suppressed below 20 mJ/pulse in order to avoid fast oxidation and ablation of the Zr surface. Positive electrostatic potentials of 100-1000 V were applied to the nickel mesh to collect charged particles. Electron currents and/or ion currents between the Zr surface and the nickel mesh were amplified using the current amplifier and averaged 50-100 times using the digital oscilloscope. The distance between the Zr rod and the nickel mesh ranged from 1.5 to 4.5 cm.

Results and Discussion

Figure 2 shows a typical time profile of photocurrents obtained by 266-nm irradiation. It was obtained at a

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distance of 4.5 cm between the Zr electrode and the nickel mesh. Since the photon energy (266 nm = 4.66 eV) is higher than a work function of Zr (ϕ = 4.05 eV), photoelectrons are expected to be ejected by one-photon ionization. The spectrum consists of two components: one is a sharp component and the other is a broad one. The former component was ascribed to photoelectrons ejected from the Zr surface.

\[ \text{Zr} + \text{hv (266 nm)} \rightarrow \text{Zr}^+ + e^- \]  
(1)

On the other hand, the latter component was ascribed to \( \text{O}_2^- \) formed by an attachment of photoelectrons to \( \text{O}_2 \). It is known that electron attachment of slow electrons to \( \text{O}_2 \) occurs via the following two-steps three-body process.\(^3\)

\[ e^- + \text{O}_2 \leftrightarrow \text{O}_2^{**} \]  
(2a)
\[ \text{O}_2^{**} + \text{M} (\text{M}=\text{N}_2, \text{O}_2) \rightarrow \text{O}_2^- + \text{M} (+ \text{energy}) \]  
(2b)
\( \text{O}_2^- \) anions are probably formed through the above two-step processes.

With increasing the electric filed from 100 to 1000 V, the sharp component increases more rapidly than the broad one due to an increase in the \([e^-]/[\text{O}_2^-]\) ratio. Figures 3 and 4 show the dependence of the peak voltage and the total recovery time on the applied voltage between the Zr rod and the nickel mesh at three different distances between the two electrodes. The peak voltage increases with an increase in the applied voltage. The threshold voltage for the detection of photocurrents increases from 0 to 200 V with increasing the distance between the two electrodes. Since the concentrations of \([e^-]\) and \([\text{O}_2^-]\) increase with decreasing the distance between the electrodes, the peak voltage becomes high at a short distance. The recovery time rapidly decreases with an increase in the applied voltage up to about 600 V and becomes nearly constant above that. This indicates that \( \text{O}_2^- \) ions are accelerated at low electric fields below about 600 V, however, the acceleration is suppressed above that due to collisions with \( \text{N}_2 \) and \( \text{O}_2 \) in air.

When laser excitation wavelength was changed from 266 nm to 532 nm, a similar time profile was observed. Since the photon energy (532 nm = 2.33 eV) is lower than a work function of Zr, photoelectrons must be ejected by two-photon ionization.

\[ \text{Zr} + 2\text{hv (532 nm)} \rightarrow \text{Zr}^+ + e^- \]  
(3)

Fig. 4. The dependence of the recovery time on the applied voltage between Zr and a charge-particle collector.

The one-photon and two-photon ionization processes of the Zr surface by irradiation of Nd:YAG laser at 266 and 532 nm are summarized in Fig. 5. Since the energies of one 266-nm photon and two 532-nm photons are 0.61 eV higher than a work function of Zr, photoelectrons with initial kinetic energies of 0-0.61 eV are ejected from the Zr surface.
They are accelerated by an electrostatic potential and decelerated by collisions with N$_2$ and O$_2$ in air. The O$_2^-$ anions are formed by collisions of slow electrons with O$_2$ atoms. The maximum electron attachment cross section of O$_2$ has been known to be about $5 \times 10^{-30}$ cm$^2$ molecule$^{-2}$ sec$^{-1}$ at an electron energy of 0.1 eV. Therefore, electrons with a kinetic energy of about 0.1 eV are expected to be effectively trapped by O$_2^-$. O$_2^-$ anions thus formed are accelerated by an electric field and collected by the nickel mesh.

Figures 6 and 7 show the dependence of the peak voltage and the total recovery time on the applied voltage at three different distances between the two electrodes at 532-nm irradiation. The relationships between the applied voltage and the peak voltage or the recovery time at 532-nm irradiation are similar to those found at 266-nm irradiation. The peak voltage increases with an increase in the applied voltage, though the absolute peak voltage is lower than that at 266-nm irradiation. The threshold voltage for the detection of photocurrents increases from 0 to about 400 V with increasing the distance between the two electrodes. The peak voltage increases with decreasing the distance between the two electrodes. The recovery time rapidly decreases with an increase in the applied voltage up to about 700 V and becomes nearly constant above that probably due to the saturation of the acceleration of kinetic energy of O$_2^-$ anions.

We found here that the Zr surface was ionized by one-photon and two-photon laser excitation processes in air. Photoelectrons ejected by the Zr surface were effectively trapped by O$_2^-$. We are planning to make a further study on photoionization processes of the Zr surface by connecting the digital oscilloscope to a microcomputer for the detailed analysis of time profile.

Fig. 6. The dependence of the peak voltage on the applied voltage between Zr and a charge-particle collector.

Fig. 7. The dependence of the recovery time on the applied voltage between Zr and a charge-particle collector.

References


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