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Surface Treatment of Polyimide Film by Pulsed UV Laser Ablation and Its Effect on the Electrochemical Characteristics

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UV laser ablation of organic polymers has been studied and many basic researches and applications have been reported.[1,2] There are several applications of polymers in laser ablations for forming electronic circuit, fabrication of micro-optical devices, microfluidic channels, and production of microholes.[3] Polyimide (PI) possess outstanding properties, such as thermo-oxidative stability, high mechanical strength, excellent electrical properties and thermal/chemical stability. Polyimide plays an important role in flexible printed circuit board, flexible display, and flexible electrode. Most of the applications of UV laser ablation of PI focused on the micropatternings,[4] preparation of microholes,[5] and microstructures for MEMS applications.[6] No work has been done about improvement of sensitivity using laser-ablated PI film as an electrode substrate.

UV laser ablations are suitable for the modification of electrode surfaces that demand more precision, speed, and simple fabrication procedure. The ablated surface of PI produces the micro structure of polyimide and enhances the sensitivity of the electrode due to increase in surface area. This technique eliminates the need for photo-masks and allows material patterning directly. In this work, ultraviolet pulsed laser ablation of polyimide film has been performed to make nano-sized structures on the polyimide surface for their application as electrochemical electrodes. To confirm the electrochemical characteristics of micro structured-polyimide, $K_3Fe(CN)_6$ is used as standard electro active materials.

The commercial PI films (Kapton[TM], DuPont, thickness = 25 μm) were irradiated in air by an externally pulsed laser operating system in the UV region using 355 nm DPSS Nd:YVO_4 laser. A pulse width FWHM (Full Width at Half Maximum) was 25 ns and the spot size of laser on PI surface was approximately 100 μm. Figure 1 shows conventional light microscopic image of the electrode (Fig. 1(a)) and the SEM images about ablated PI surface (Fig. 1(b)). The UV laser was irradiated onto the head part of PI surface (4.0 × 4.0 mm) as a sensing area for the voltammertic measurements and another part of tail was used without laser ablation (Fig. 1(a)). After laser ablation of polyimide film, all surfaces of PI are deposited with thin layer of Pt by vacuum deposition to give a conducting surface. A portion of PI surface was covered with nail-polish insulating layer, leaving on both ends for defining the working electrode and the electrical

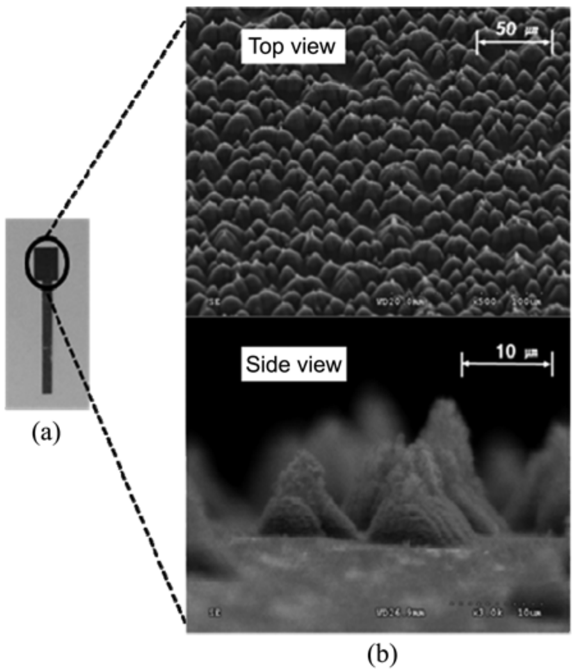

Figure 1. (a) Image of polyimide based electrode and (b) SEM images of its surface applying UV laser ablation.

contact. Unlike most commercial insulators, this type of insulator is compatible with the low-temperature curing and is stable in aqueous solution. At the radiation influence of 94.5 mJ/cm^2, densely packed cones are formed in 10 μm size of average height and base diameter. Also, the numbers of cones decreases with the lower radiation influence than 94.5 mJ/cm^2.

Cyclic voltammetry (CV) is a very useful electrochemical technique to test new electrode because its principle and theory have been well established. The CV is characterized by important parameters such as the anodic and cathode peak potentials and peak currents. The $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple is well-behaved both chemically and electrochemically as a reversible redox system in electrochemistry. Prior to the test for voltammetric behavior for $K_3Fe(CN)_6$, pretreatment of platinum coated PI (PI/Pt) surface was performed by potential cycling from −0.2 V to 1.4 V (*vs* Ag/AgCl) in 0.1 M H_2SO_4 solution. Cycling the electrode potential

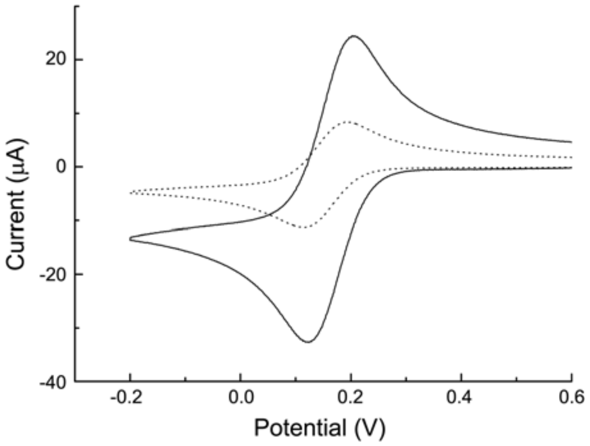

Figure 2. Cyclic voltammograms of plain Pt/PI (dotted line) and laser ablated Pt/PI (solid line). Scan rate = 100 mV/sec, concentration of $K_3Fe(CN)_6$ = 1.0 mM.

between limits at which the platinum surface is oxidized and reduced has proven to be effective in the removal of adsorbed impurities on Pt surface. A typical cyclic voltammogram is shown in Figure 2 for plain (without ablation on PI surface) and laser ablated PI/Pt in a solution of 1.0 mM $K_3Fe(CN)_6$ as the electroactive species in 0.1 M KNO_3 in water as the supporting electrolyte. The redox peak currents of ablated PI/Pt were higher than that of plain PI/Pt. This is attributed to the increase in electrochemical sensing area of ablated PI/Pt after laser ablation. The electroactive surface area was calculated by Randle-Sevcik equation at various scan rates using cyclic voltammetry. For 1.0 mM of $K_3Fe(CN)_6$, the experimental value of electroactive surface area for ablated PI/Pt is 1.36 cm^2. The geometrical area of plain PE/Pt is 0.64 cm^2. The larger electroactive surface area in ablated PI/Pt than plain PI/Pt supports the larger $K_3Fe(CN)_6$ redox peak current shown in Figure 1. The relationship to concentration is particularly important in quantitative electro analytical chemistry. So, the increase in redox currents at ablated PI/Pt can be used for improving the sensitivity during electroanalyses. The values of anodic and cathodic peak current for $K_3Fe(CN)_6$ are almost same and the ratio of two currents is unity. The reduction and oxidation peak potentials of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple are +0.131 V and +0.192 V, respectively. The half-wave potential of the redox couple was +0.161 V that comparable as reported value.[7] The potential difference (ΔE_p) of two redox peaks is 60 mV, which indicates a typical ΔE_p value for reversible one-electron process of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple. To check the electro activity of PI/Pt electrode, the CVs were performed for $K_3Fe(CN)_6$ using commercial Pt disk electrode (diam = 2 mm). The redox peak potentials of two electrodes were same at same concentration of $K_3Fe(CN)_6$. The current effect of laser ablated Pt/PI electrode was also tested for the reduction of H_2O_2 using cyclic voltammetry in a pH 7.4 phosphate buffer solution. In living organisms, H_2O_2 is well-known for cytotoxic effects and regulating biological processes. H_2O_2 is also a side product generated from some biochemical reactions catalyzed by enzymes. Therefore, the study on H_2O_2 detection is of practical significance for the development of electrochemical biosensors. Figure 3 depicts the increase in reduction peak current with the increase in H_2O_2 concentration at +0.09 V. The reduction current of ablated PI/Pt is almost two times higher than plain PI electrode due to increase in surface area by laser ablation. The detection limits of H_2O_2 detection for plain and laser ablated Pt/PI were 48.6 and 20.5 μM, respectively.

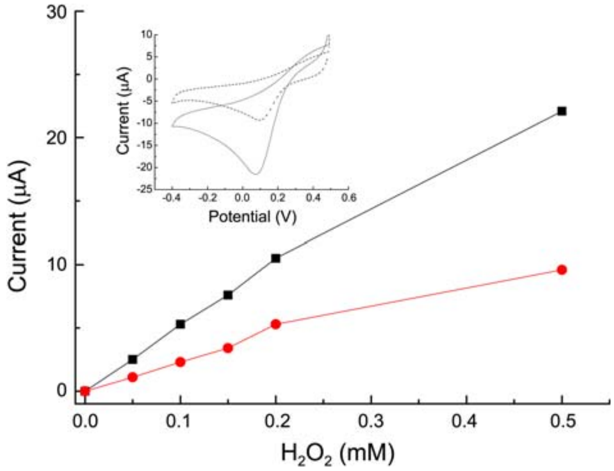

Figure 3. Current dependency for reduction of H_2O_2 at the plain Pt/PI (●) and laser ablated PI/Pt (■) using cyclic voltmmetry. Scan rate = 100 mV/sec. Inset shows CVs of 0.5 mM of H_2O_2 for plain Pt/PI (dotted line) and laser ablated Pt/PI (solid line).

In summary, ultraviolet pulsed laser ablation of polyimide film has been used to change the surface morphology for the application as an electrochemical electrode. Densely packed cones are formed on PI surface after UV irradiation which results in increase of surface area. To confirm the electrochemical sensitivity of micro structured-polyimide film, $K_3Fe(CN)_6$ and H_2O_2 are used as an electro active materials. The sensitivity of ablated PI/Pt is higher than that of plain PI/Pt due to increase in surface area by laser ablation.

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