

## Advanced Laser Science Research Section

T. Nakajima, Associate Professor

## 1. Introduction

We use lasers to fabricate the functional materials and also to probe the dynamics without perturbing the various processes. This year we have developed three different techniques. The first one is to probe the bubble dynamics of hydrogen evolution reaction through alkaline water electrolysis, and the second one is to fabricate the optical elements. The third one is to obtain the high quality holes and lines, which are the most elementary unit structures for laser micromachining with unprecedented quality.

## 2. Role of the surface morphology of the electrodes to form hydrogen and oxygen bubbles during water electrolysis

Hydrogen evolution via water electrolysis is one of the promising candidates for renewable energy production. Toward efficient hydrogen evolution, not only the catalysis development but also the morphological design of the electrode surface to attain the high surface-area-to-volume ratio is important. However, bubbles sitting on the electrode surface reduce the active surface area and increase the ohmic resistance between electrolyte and electrode interface, and it is important to find the optimal morphology of the electrode surface so that the bubble detachments occur soon after their formations with a minimal duration on the electrode surface. Our previous study has revealed that the hydrogen bubbles are preferentially formed at the sites with pits or crevices on the electrode surface. A natural question is whether those sites also serve as the forming sites of oxygen bubbles when the polarity of the electrode is reversed.

In this study, we carry out the comparative study on the forming sites of hydrogen and oxygen bubbles using the identical Ni electrode with a single laser-induced microstructure by reversing the polarity of the electrode, and we take the movie of the bubbles on the electrode surface during the electrolysis (Fig. 1(a)). The bubbles in the vicinity of the electrode surface are illustrated in Fig. 1(b). Representative optical images of hydrogen and oxygen bubbles during hydrogen as well as oxygen evolution reaction (HER and OER) are shown on the left side of Fig. 1(c), where the hydrogen and oxygen bubble forming sites are marked by thick-white and thin-blue circles, respectively. It is very interesting to point out that all the forming sites of

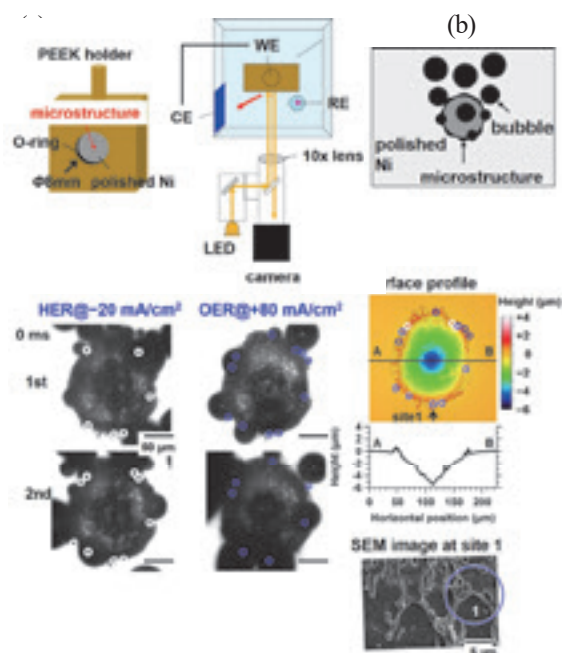


Fig. 1 (a) Setup for the water electrolysis and bubble measurements. (b) Schematic of bubbles on the microstructured Ni electrode. (c) Representative optical images of hydrogen and oxygen bubbles forming at the microstructure, false-colored surface profile, and the SEM image at site 1 indicated in the surface profile.

hydrogen bubbles are found only at the periphery of the microstructure, while those of oxygen bubbles are found not only at the periphery of the microstructure but also on the flat area around the microstructure. This suggests that, although the shallow surface structure is preferred to form bubbles and the local surface morphology plays a crucial role for hydrogen bubbles, it plays a lesser role for oxygen bubbles and some other factors such as local convection play some roles. Those findings are very important to design the electrode surface structure toward efficient HER.

## 3. Facile fabrication of optical diffusers by ablation-assisted nanosecond laser micromachining

Optical diffusers are essential elements to alter the spatial distribution of incident light, and frequently used as essential components in optoelectronic

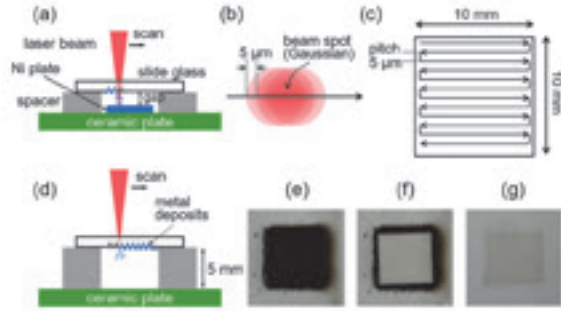


Fig. 2 Change of the diameter of fabricated holes on the Ni substrates with and without Ni films as a function of laser fluence.

devices. It is known that there are two approaches to fabricate the optical diffusers. The first one is to produce micro/nanostructures on the surface of a transparent glass substrate by direct laser writing, and the second one is to produce appropriate patterns through the introduction of fillers or lithography to a transparent polymer film through the wet chemical processes.

For the direct laser writing of micro/nanostructures at the surface of a transparent glass substrate an ultrashort laser is usually employed. It is practically impossible to structure the transparent glass with nanosecond laser in the visible or near-infrared wavelength range. One way out of this is to use energetic fragments to etch glass, and we undertake ablation-assisted laser micromachining of glass substrate by nanosecond laser pulses in the near-infrared range. The fabrication procedures of optical diffusers are shown in Fig. 2. Briefly, we ablate the Ni plate which is placed behind the slide glass with a small ( $<1$  mm) gap with nanosecond laser pulses (40 ns at 50 kHz) with various laser powers at the scanning speeds of 250 to 2000 mm/s (Fig. 2(a)-(c)). Then, we remove the Ni plate and perform laser cleaning to remove debris from the slide glass (Fig. 2(d)-(g)). This way, we do not have to introduce any wet chemical cleaning process to fabricate the optical diffuser. A representative surface morphology of the diffuser and beam profile through it is shown in Fig. 3. The advantage of the developed technique is that it is very quick and efficient without any wet process. This demonstrates that cost-effective nanosecond laser can be a convenient tool for laser micromachining of transparent materials.

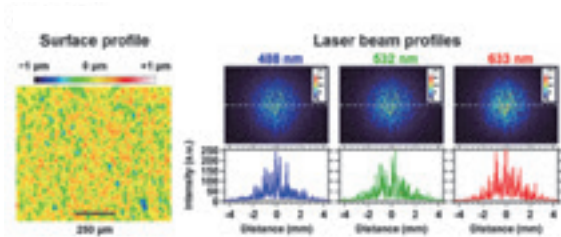


Fig. 3 Representative surface morphology of the fabricated diffuser and beam profile through it.

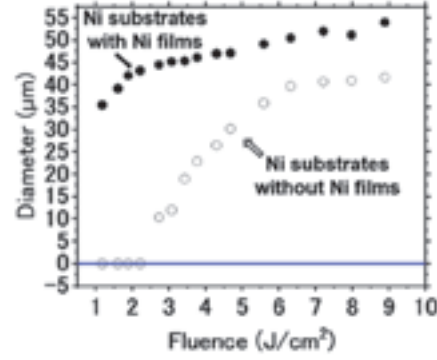


Fig. 4 Change of the diameter of fabricated holes on the Ni substrates with and without Ni films as a function of laser fluence.

#### 4. Fabrication of depth-controlled high quality holes and lines on a metal substrate by nanosecond laser pulses

It is widely believed that an expensive femtosecond laser is necessary to fabricate high quality holes with very little ablation rims, while the use of inexpensive nanosecond laser suffers from the formation of pronounced ablation rims. It is not always so only if we can somehow suppress the heat problems. Our idea to realize such situation is to introduce a thin metal film on a metal substrate, and selectively blow out the film with laser pulses of modest fluence. This is possible, as we show in Fig. 4 for a Ni substrate with a Ni film of 80 nm thickness, because the ablation threshold of a metal film on a metal substrate is much lower than that of the bare metal substrate.

After ensuring that we can selectively blow out the Ni film while the Ni substrate is intact, we perform nanosecond laser micromachining of Ni substrate with a Ni film of 80 nm thickness to fabricate the high quality hole and line (Fig. 5), which exhibit the very flat bottoms without notorious rims. This demonstrates that the metal substrate with a metal film is a nice workpiece to fabricate high quality holes and lines by nanosecond laser micromachining.

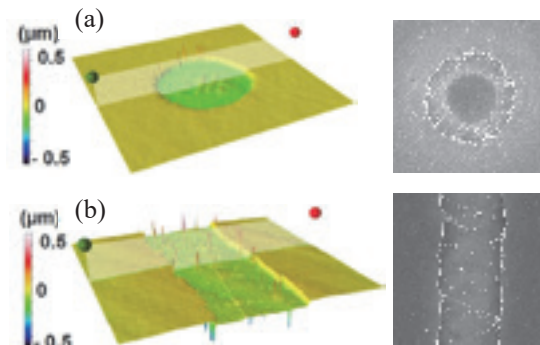


Fig. 5 Morphologies and SEM images of the fabricated (a) hole and (b) line on the Ni substrates with a Ni film.

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中嶋隆, (公財) 京都大学教育研究振興財団, 水電解水素製造の高効率化: レーザー科学からのアプローチ

中嶋隆, (公財) 天田財団, 高繰り返しナノ秒パルスレーザーを用いた革新的レーザー除染技術の開発

## Publications

W. Rong, K. Ando, T. Nakajima, Facile fabrication of optical diffusers by ablation-assisted nanosecond laser micromachining of glass substrates, *Optics and Lasers in Engineering*, 167, 107621, 2023

K. Ando, Y. Uchimoto, T. Nakajima, Comparative study of bubble forming sites at the laser-induced microstructure on a Ni electrode during hydrogen and oxygen evolution reactions, *International Journal of Hydrogen Energy*, 49, 449-457, 2023

K.Sota, K. Ando, T. Nakajima, Fabrication of depth-controlled high-quality holes and lines on a metal surface by nanosecond laser pulses at 1064 nm, *International Journal of Advanced Manufacturing Technology*, 2023

K. Sota, K. Ando, H. Zen, T. kii, H. Ohagaki, T. Nakajima, Morphological study of depth-controlled high quality holes and lines fabricated on a metal substrate with a thin metal film by picosecond laser pulses, *Optics and Laser Technology*, 175, 110853, 2024

## Presentations

T. Nakajima, Hydrogen evolution efficiency with laser-textured electrodes, The 14th International Symposium of Advanced Energy Science, 京都大学宇治キャンパス, 2023.9.1