REAL-TIME OBSERVATION OF SURFACE CHEMICAL REACTIONS WITH FEL-INDUCED PHOTOELECTRON EMISSION MICROSCOPY

H.Ogawa#, K. Yamada, N. Sei, K. Watanabe, M. Yasumoto
Research Institute of Instrumentation, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

Abstract

At AIST, we have been making an effort to obtain FELs with an ultra-wide wavelength range from the vacuum ultraviolet (VUV) to the infrared (IR) based on a compact storage ring NIJI-IV. Recently, performance of the NIJI-IV FEL was improved at the deep UV (DUV) around 200 nm and it became possible to make real-time observation of chemical reactions on the transition metal surfaces using the photoelectron emission microscopy (PEEM). To observe dynamic behavior of the chemical reactions in detail, the FEL-PEEM system is being improved by optimizing experimental conditions. The performance of the system and the experimental results are presented.

INTRODUCTION

To extend the FEL wavelength from VUV to IR, the NIJI-IV FEL system has been modified. The replacement of NIJI-IV vacuum chambers as well as installation of thin sextupole magnets has been performed in order to increase FEL gain and lasing wavelength was shortened to be 198nm up to now [1-3]. And a 3.6-m optical klystron ETLOK-III was installed into the north straight section of the NIJI-IV for lasing in the IR region [4].

Recently, we improved performance of the NIJI-IV FEL system in the DUV region by optimization of the transmittance of the output coupler for the optical cavity and the increasing stored electron-beam energy. As a result, the output FEL power around 200nm increased by an order magnitude than before [5]. The average output FEL power is 0.5mW and the laser-line width is 0.08nm. This enables us to make a real-time observation of the chemical surface reaction using DUV FEL in combination with a photoemission electron microscopy (PEEM). In the previous report [5], the spatial and temporal resolutions of the NIJI-IV FEL-PEEM system were estimated to be ~300nm and 33ms, respectively. In this work, dynamics of catalytic CO oxidation on a transition metal surface is observed in more detail than previous work [5] by changing the experimental conditions.

THE NIJI-IV FEL –PEEM SYSTEM

The NIJI-IV is a compact storage ring whose circumference is 29.6m and is operated at a beam energy of 340MeV for the FEL-PEEM experiments. The FEL at a wavelength of 202nm emitted from a 6.3-m optical klystron ETLOK-II is transported to the experimental room through the air and was reflected by a flat aluminium mirror and focused onto the sample surface as shown in Fig.1. The electronic images of the PEEM system (STAIB Instrumente, type 350) are magnified by a system of electrostatic lenses and amplified by a micro channel plate (MCP) and are projected onto a phosphor screen. The focused images on the florescent screen are recorded by a CCD camera and stored on HDD recorder. The detail of the experimental setup is described in Ref. [5].

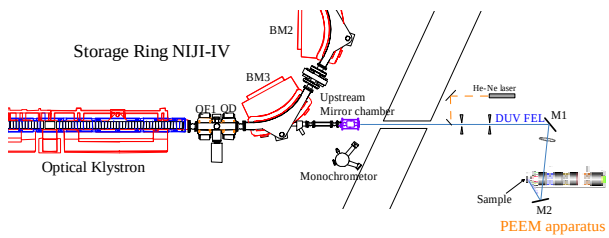

Figure 1: Schematic view of the NIJI-IV FEL-PEEM system.

OBSERVATION OF CO OXIDATION ON THE TRANSITION METAL SURFACE

In this work, the catalytic CO oxidation ($2CO + O_2 \rightarrow 2CO_2$) on a Pd(111) single crystal was studied by introducing CO and O_2 gases. The CO oxidation on the transition metal surfaces has been investigated in many works [7-10]. It is known that on the surface CO adsorbs in a molecular form, while O_2 adsorbs dissociatively. The product molecule CO_2 immediately leaves the surface as soon as it is formed. The reaction only proceeds between adsorbed particles via Langmuir-Hinshelwood (LH) mechanism.

The reaction depends sensitively on the experimental conditions (i.e. crystal temperature, gas pressure etc.). Hence, first of all, it is needed to search good conditions for the catalytic CO oxidation. During the measurement, the surface was irradiated by an FEL or spontaneous emission from ETLOK-II at a wavelength of 202 nm. It is convenient for the experimental condition search to use the spontaneous emission because the life time of the spontaneous emission is better than that of FEL. In this paper, we report on the surface observation obtained using the spontaneous emission as a DUV light source.

#ogawa.h@aist.go.jp

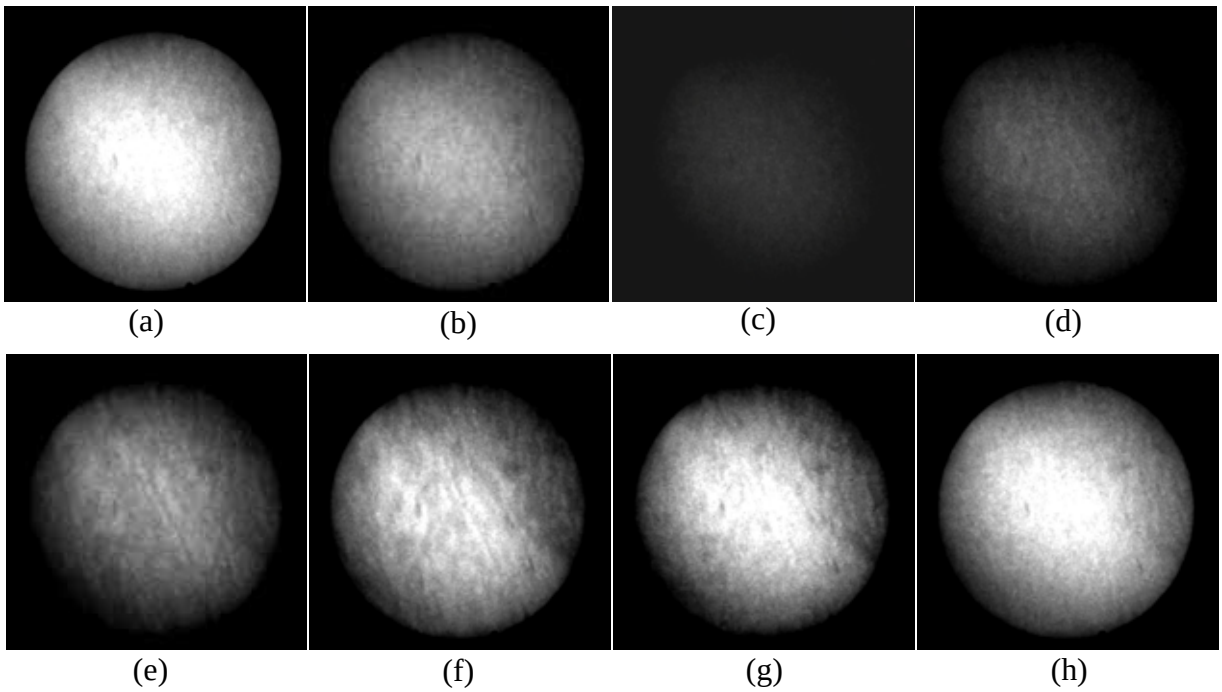

Figure2: The PEEM images for a Pd(111) surface at 340K after cleaning (a), a CO-adsorbed surface exposed to 2×10^{-5} Pa CO (b) and (c), and surface reaction of CO and O_2 (d)-(h) with 8×10^{-5} Pa O_2 exposure. Image size 200μm in diameter.

Before the PEEM experiment, a routine preparation procedure was performed by cycles of Ar^+ sputtering, annealing and oxygen treatment to obtain a clean surface.

Figure2 shows preliminary data of a series of snapshots for PEEM images on a Pd(111) surface at 340K. The stored beam current was between 10 and 8.5 mA. PEEM image size is 200 μm in diameter. In (a) an image of the photoelectrons emitted from the clean surface. Then the Pd(111) surface is exposed to 2×10^{-5} Pa CO. One can see in (b) and (c) that the brightness of the image is reduced through the adsorption of CO molecules over the whole surface since the CO coverage rises the work function, and the surface was completely covered with CO in (c). After stopping the CO exposure, a CO precovered surface is exposed to 8×10^{-5} Pa O_2. The images of (e)-(h) were taken at (e) t=4s, (f) t=8s, (g) t=12s, (h) t=19s after introducing oxygen gases in (d). A complicated black and white domain appeared in (e) and (f). This reflects on the difference of photoelectron yield which depends sensitively on the local work function. Several bright islands seen at the center of (f) seems to be the areas where the adsorbed CO molecules are desorbed to form CO_2 through chemical reaction with O_2. Finally the bright area was spread over whole area of the center in (h).

CONCLUSION

We are developing the NIJI-IV FEL-PEEM system for real-time observation of chemical reactions on the transition metal surfaces. The catalytic CO oxidation on the transition metal Pd(111) single crystal surface was investigated using PEEM combined with NIJI-IV DUV light source. The PEEM experiment with DUV FEL is now in progress. The narrow line width of FEL would enable us to obtain a high image contrast.

ACKNOWLEDGEMENTS

This study was financially supported by the Budget for Nuclear Research of the Ministry of Education, Culture, Sports, Science and Technology, based on the screening and counseling by the Atomic Energy Commission of Japan.

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