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Dynamics of Material Surface Changes due to Hydrogen Plasma Exposure

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Abstracts We investigate the work function changes of C12A7-electride after the termination of hydrogen plasma exposure. Photoelectric current from C12A7-electride decreases rapidly after the termination of plasma exposure for a time constant of 1–3 min. By comparing the observation results at high temperatures (500–400 degrees C) and those at room temperature (~45 degrees C), possible interpretations of this phenomenon are discussed.

1. Introduction

It has been known that low-work-function material is needed for efficient production of hydrogen negative ions (H^-) on plasma electrodes in H^- sources, and for reduction of co-extracted electrons. It has been known that a half monolayer (or less) Cs coverage on a Mo surface shows the minimum work function, but it can be decreased more when the surface is immersed in a hydrogen plasma [1 - 4].

As one of the promising candidate PE materials for Cs-free negative hydrogen ion sources, a new material, C12A7-electride [5, 6] has been studied [7], recently. In order to clarify the mechanism that changes negative ion yields and the work function of C12A7-electride due to plasma exposure, a series of experiments were carried out using a surface-produced negative ion measurement system and a photoelectron yield spectroscopy system installed on the diffusion plasma reactor at PIIM Aix-Marseille University [8, 9, 10].

2. Experimental set-up and measurement results

The plasma was generated at 2 Pa by capacitive coupling from an external antenna using an 1600 W, 13.56 MHz generator (Huttinger PFG 1600 RF). The sample holder lay in the center of the diffusion chamber, which was separated from the driver region by a metallic mesh. The sample could be biased negatively by an external DC power supply, and could be heated by a resistive heater embedded inside the sample holder. Without external heating, the sample temperature was maintained below 60 degree because the impinging ion flux is low enough. The sample holder could be rotated by 180 degree and facing towards a Hiden-EQP300 mass spectrometer equipped with an energy filter, or towards the photo-emission yield spectroscopy (PYS) system to measure the work function. As in shown in Fig. 1, the PYS setup consisted in a 300 W Xenon lamp combined with a Zolix monochromator to generate a monochromatic light. The photon beam was focused to form a 3-mm-diameter spot on the grounded sample. The light was chopped by a rotating chopper and its wavelength could be scanned from 200 to 600nm (6 to 2 eV), and for each wavelength the sample current was acquired by a Keithley 6482 ammeter and sent to a computer through a MFLI lock-in amplifier giving the so-called PYS curve.

A full scan takes about 170 seconds, which can be diminished by scanning a narrow wave length range. Figure 2 shows an example of photoelectron current versus wavelength scan. This acquisition took about 90 seconds.

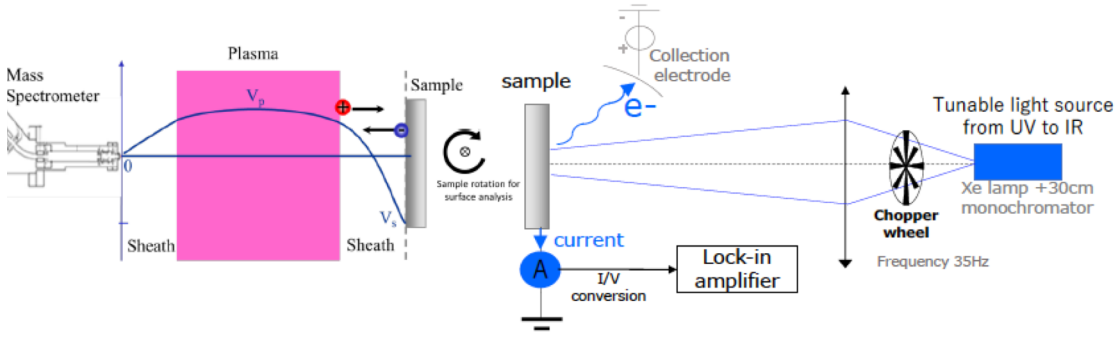
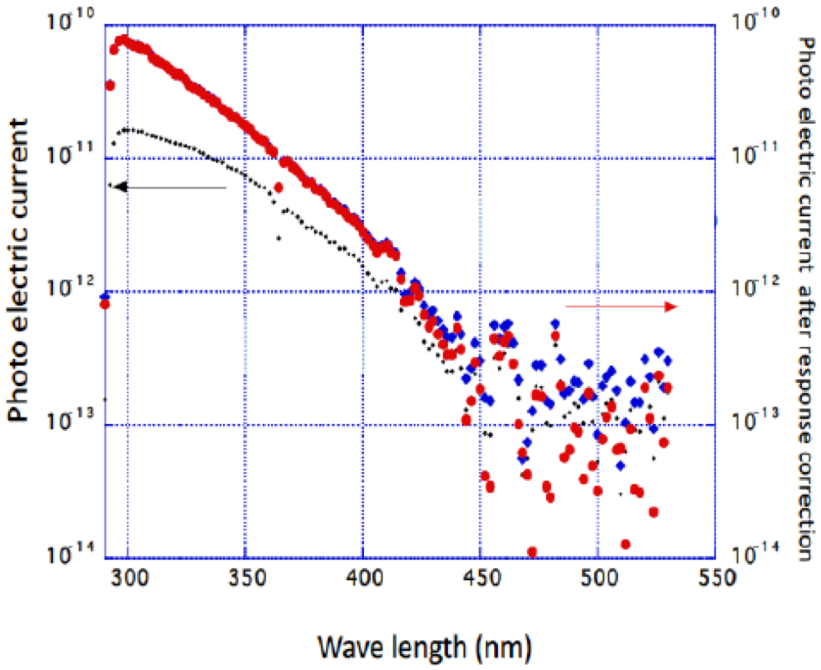


Fig. 1 Schematic view of measurement system, presented by G Cartry, at ICPIG XXXV (July 9 - 14, 2023, Egmond aan Zee, The Netherlands). Details are described in the text.



A simplified version of the Fowler relation, such as the following, is often used to estimate a work function value $\boldsymbol{\phi_w}$.

$$Y \propto T^2\mu^2 \propto (h\nu - \phi_w)^2 \qquad \text{Eq. (1)}$$

where

$$\mu = \frac{h\nu - \phi_w}{k_B T}. \qquad \text{Eq. (2)}$$

and Y is the photoelectron yield. This relation can be used when $\mu > 5$. However, Lange et al. has shown that the photoelectric yield should be fitted to a power law with variable exponent, n, in case of the presence of an adsorbate on a metal surface [11].

$$Y \propto (h\nu - \phi_w)^n \qquad \text{Eq. (3)}$$

In order to catch the rapid change of work function and extrapolate towards the value of the plasma phase, a monochromatic lights of various wave length were injected, and the photoelectric current changes after each D_2 plasma termination were measured. We reported the results of 380 nm, 400 nm, or 420 nm injection, and assuming Eq. (3) and the exponent "n" of 2.7. The work function was calculated from the photoelectric currents of 3 photon energy by least-squares fitting, and as shown in Fig. 3, it was found that the work function values were gradually increasing after the plasma termination, but by extrapolating to the plasma termination values are about 2.4–2.5 eV [12,13].

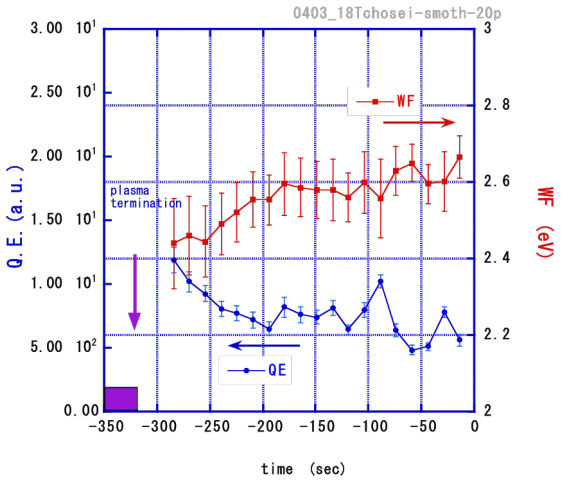


Fig.3 Changes of work function calculated by least-squares fitting to the photoelectric currents from the injection of monochromatic light of 380 nm, 400 nm, and 420 nm, after termination of 150 W D2 plasma.

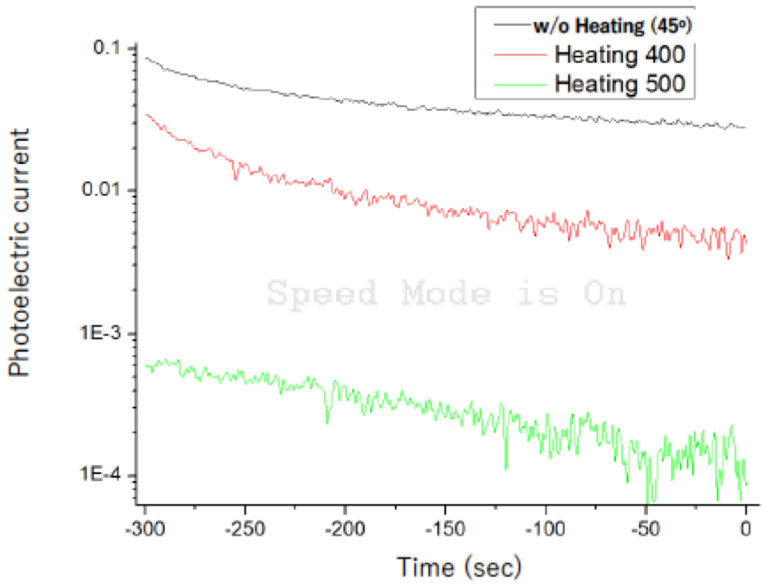


Fig. 4 Changes of photoelectric current at 290 nm injection, after the 150 W, 2 min. D_2 plasma termination. The black line shows the results without heating (45°C), the red line after heating to 450 (450°C – 300° C), and green line after heating to 500 (500°C – 350° C).

In the present work, the effect of surface temperature on the reversion phase of photoelectric current are studied. Fig. 4 shows changes of photoelectric current at 290 nm injection, with heating and after heating. Remind that after heating, the target temperature was also lowering gradually with speed about 0.5 deg./sec.

3. Discussions and Conclusion

Possible interpretation of work function lowering in a H/D plasma might be effects of hydrogen atoms (H^0 or D^0). (a) They can react with impurities on the C12A7-electride surface, such as oxygen, O_2^-, O^-, and/or OH^-, remove them, and a clean electride surface may appear. (b) Hydrogen atoms on the top surface might change the property. (c) Another interpretation is the intrinsic change of C12A7-electride. When the hydrogen plasma terminates, the influx of hydrogen atoms is terminates fast, because the time constants of recombination processes are much shorter than few seconds. Impurities cleaning by the plasma and re-adsorbing after the plasma is not probable since WF is increasing after plasma at high temperature while it is probably not possible to readsorb impurities at high temperature. Then the interpretation (b) might be the most likely. Present results of temperature effect provide a valuable clue to study the chemical desorption process of hydrogen on the electride.

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