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Improved Pumping Speeds of Oxygen-Free Palladium/Titanium Nonevaporable Getter Coatings and Suppression of Outgassing by Baking under Oxygen

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1 Introduction

Nonevaporable getter (NEG) coating is a technique in which the inner walls of a vacuum chamber are coated with a thin film of a NEG material [1, 2]. We recently developed a new NEG coating consisting of an oxygen-free thin film of Ti covered with a thin film of Pd, which we named the 'oxygen-free palladium/titanium (Pd/Ti) coating' [3-6]. Here, we report an effective and simple method for removing carbon contamination from the Pd/Ti surface to improve the pumping speeds of oxygen-free Pd/Ti for H_2 and CO, and to reduce the partial pressures of H_2, CO, H_2O, and CH_4 [7].

2 Experiment

The oxygen-free Pd/Ti film was deposited on SS304L substrates or a SS304L chamber under clean ultrahigh vacuum (UHV) conditions. The thicknesses of the Pd and Ti thin films were approximately 50 nm and 1.3 μm, respectively. X-ray photoelectron spectroscopy (XPS) measurements of oxygen-free-Pd/Ti coated substrate were carried out at room temperature by using *p*-polarized SR light with a photon energy (*hv*) of 700 eV at BL-13B of Photon Factory. The surface morphologies of the unheated and UHV-heated oxygen-free Pd/Ti samples were observed by scanning electron microscopy (SEM). Total and partial pressure curves of the oxygen-free Pd/Ti coated chamber were measured using the apparatus shown in Fig. 1a. Before, during, and after UHV or O_2 baking, the total and partial pressures in the oxygen-free Pd/Ti coated chamber with the TMP were measured by using a quadrupole mass spectrometer and the apparatus shown in Fig. 1b. Pumping speeds of the oxygen-free Pd/Ti coated chamber for H_2 or CO were measured by the orifice method [8] using the apparatus shown in Fig. 1c.

3 Results and Discussion

Samples of oxygen-free Pd/Ti that were unheated, heated in UHV at 150 °C for three hours, or heated at 150 °C for three hours under an O_2 pressure of 1.3×10^{-4} Pa were analyzed by XPS. We found that carbon contamination decreased to an extent on heating in UHV, but decreased considerably on heating in O_2 (Figs. 2 and 3). The graphite or graphene coverage of the unheated sample was estimated to be 0.9 ML, whereas those of the UHV-heated and O_2-heated samples were estimated to be 0.3 and 0.04 ML, respectively.

Figures 4a and 4b show SEM images of the Pd surface of the unheated and UHV-heated (at 150 °C for 12 hours) oxygen-free Pd/Ti samples. The Pd surface of the unheated sample had an uneven structure with irregularities of several tens to several hundreds of nanometers and numerous steps, whereas the surface of the UHV-heated sample had a leaf-like structure with relatively large flat surfaces. These results are consistent with the XPS spectra, which suggest that the number of less-coordinated Pd atoms decreases after heating.

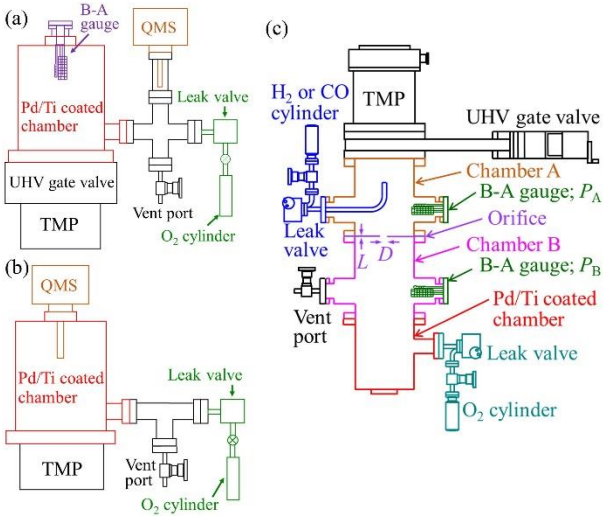

Fig. 1: Schematics of the apparatus for measuring (a) the total and partial pressures in the coated chamber before and after valve closure; (b) the total and partial pressures in the coated chamber without valve before, during, and after UHV or O_2 baking; and (c) the pumping speeds for the coated chamber. Reproduced from Ref. 7, with the permission of AIP Publishing.

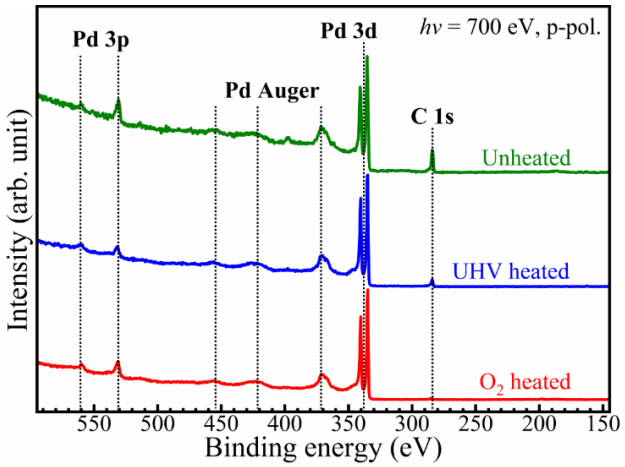

Fig. 2: Wide-scan XPS spectra of the unheated, UHV-heated, and O_2-heated oxygen-free Pd/Ti samples. Reproduced from Ref. 7, with the permission of AIP Publishing.

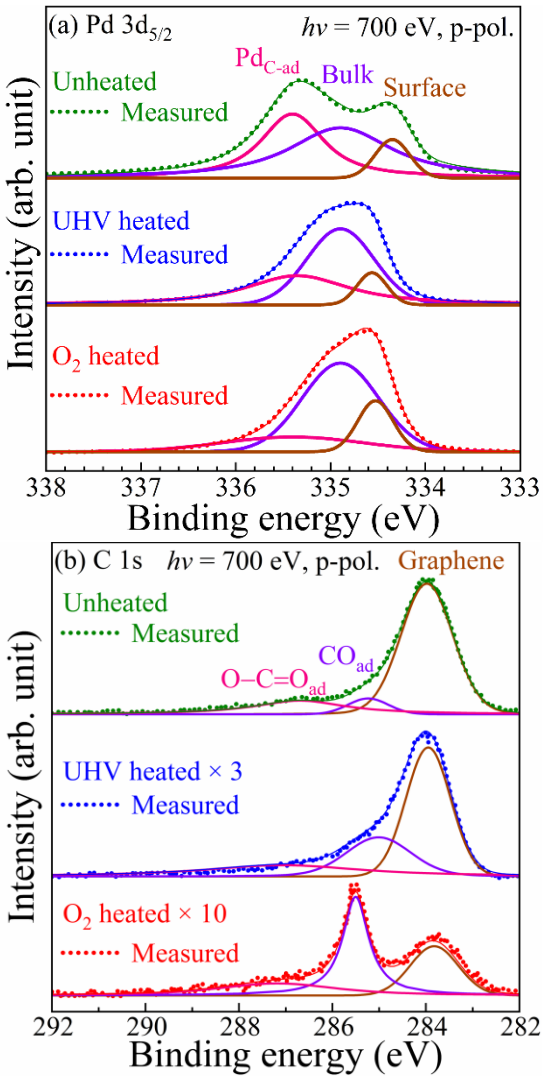

Fig. 3: Measured, fitted, and deconvoluted peaks of (a) Pd $3d_{5/2}$ and (b) C 1s. Reproduced from Ref. 7, with the permission of AIP Publishing.

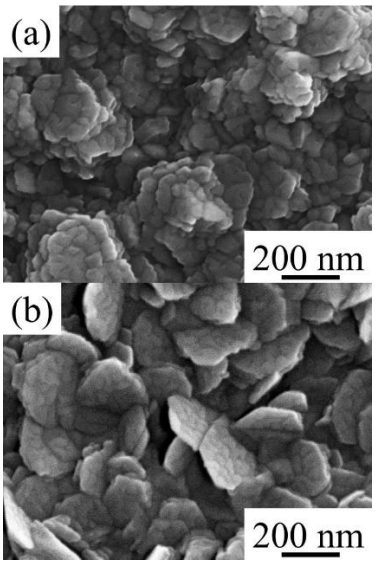

Fig. 4: SEM images of the Pd surface of the (a) unheated and (b) UHV-heated oxygen-free Pd/Ti samples. Reproduced from Ref. 7, with the permission of AIP Publishing.

Figure 5 shows the total and partial pressures of the oxygen-free Pd/Ti coated chamber before and after valve closure after UHV or O_2 baking at 150 °C for 12 hours. In the case of UHV baking, after the valve closure, the total pressure was 4.2×10^{-6} Pa and the partial pressures of H_2 and CO increased to 1.4×10^{-7} and 8.9×10^{-7} Pa, respectively, in five hours. On the other hand, in the case of the O_2 baking, the corresponding pressures were improved to 1.0×10^{-6}, 3.6×10^{-8}, and 5.8×10^{-8} Pa in five hours. These improvements are much larger than would be expected from the graphite or graphene coverage (0.3 ML for UHV-heated and 0.04 ML for O_2-heated samples). The results therefore indicate that removal of carbon contamination not only improves the pumping speeds of oxygen-free Pd/Ti thin films for H_2 or CO, but also suppresses outgassing from the chamber.

Figure 6 shows the partial pressures in the oxygen-free Pd/Ti coated chamber before, during, and after UHV and O_2 baking. During UHV baking, the partial pressure of CO_2 was 1×10^{-6} to 2×10^{-8} Pa, whereas that during the O_2 baking was 6×10^{-6} to 3×10^{-7} Pa. The partial pressures of CO_2 during the O_2 baking were larger by a factor of 6−15 than those during the UHV baking. This suggests O_2 reacts with the carbon on the Pd surface to form CO_2. During UHV baking, the partial pressure of H_2O was 2×10^{-5} to 9×10^{-7} Pa, whereas that during the O_2 baking was 3×10^{-5} to 1×10^{-6} Pa. The partial pressures of H_2O during the O_2 baking was larger by a factor of 1.1−1.5 than that during the UHV baking. This result suggests that H on Pd surface was removed by catalytic chemical reactions such as

$$2H_{ad} + \frac{1}{2}O_2 \xrightarrow{Pd_{cat}} H_2O$$

during O_2 baking. Removal of H and C adsorbed on the inner surfaces of the chamber seems to be responsible for the reduction of the partial pressures of H_2, CO, H_2O, and CH_4 after the O_2 baking.

Figure 7 shows the measured pumping speeds of the oxygen-free Pd/Ti coated chamber for H_2 and CO as a function of the pumped quantity after UHV or O_2 baking. The apparatus used is shown in Fig. 1c. Pumping speeds for H_2 after UHV or O_2 baking were measured as 510–120 and 990–400 L s^{-1}, respectively in the pumped-quantity range 0.01–10 Pa L. Those for CO were determined to be 960–40 and 1250–140 L s^{-1}, respectively in the pumped-quantity range 0.005–1 Pa L. The initial pumping speeds were improved by factors of 1.9 for H_2 and 1.3 for CO. These results indicate that O_2 baking improves the pumping speeds for H_2 and CO owing to removal of carbon contaminants. These results demonstrate that O_2 baking is useful for removing the carbon contaminants from oxygen-free Pd/Ti and for recovering pumping speeds of oxygen-free Pd/Ti for H_2 and CO.

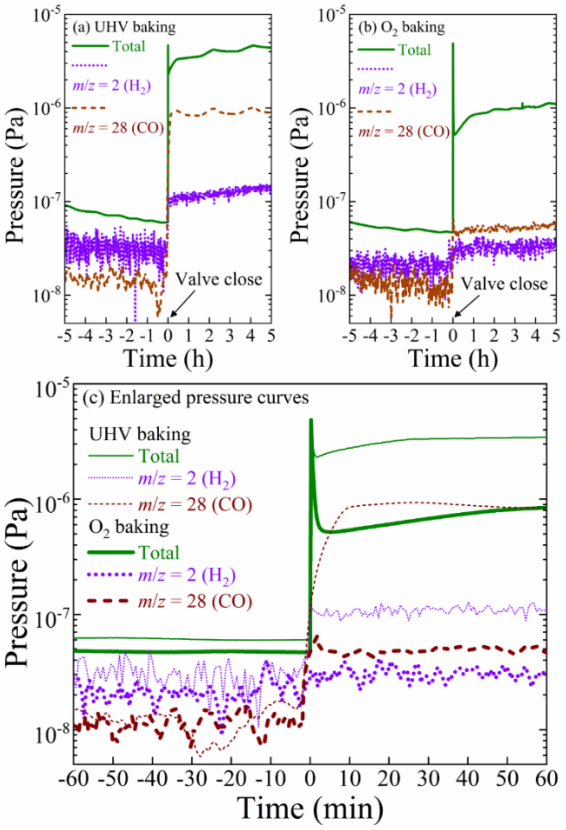

Fig. 5: Total and partial pressure curves of the oxygen-free Pd/Ti coated chamber before and after closing the pneumatic UHV gate valve 12 hours after (a) UHV or (b) O_2 baking at 150 °C for 12 hours. The time of closure of the valve is taken as the origin of the time axis. (c) Enlarged pressure curves before and after valve closure. The dominant gas species are indicated in parentheses. Partial pressures of residual gases other than m/z = 2 (H_2) or m/z = 28 (CO) are not shown. The apparatus used is shown in Fig. 1a. Reproduced from Ref. 7, with the permission of AIP Publishing.

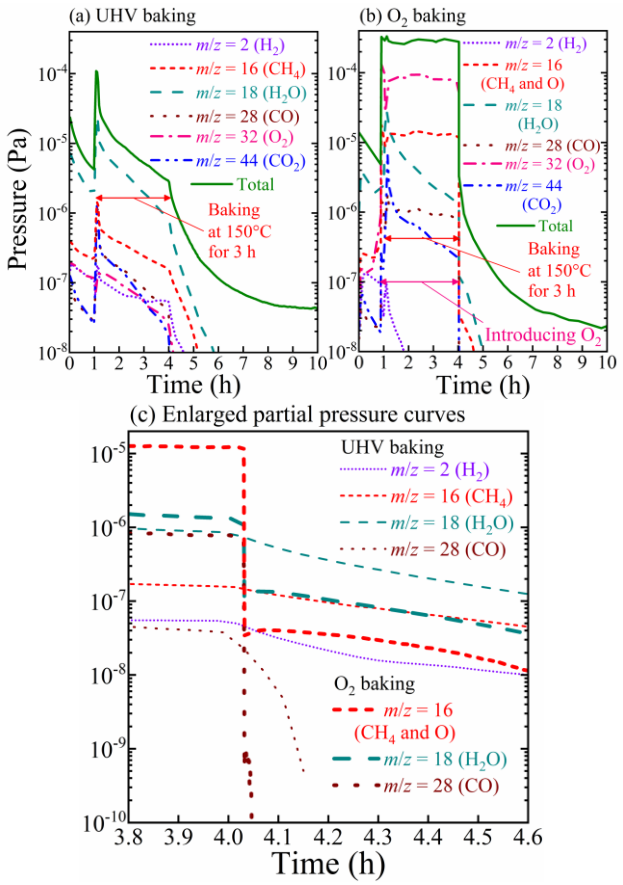

Fig. 6: Partial-pressure measurements in the oxygen-free Pd/Ti coated chamber during (a) UHV or (b) O_2 baking. Five minutes after starting RP, the TMP was started, and the QMS was started about 13 minutes later. The time when pressure measurements commenced is taken as the origin of the time axis. (c) Enlarged partial pressure curves before and after the UHV or O_2 baking off. The dominant gas species are indicated in parentheses. The apparatus used is shown in Fig. 1b. Reproduced from Ref. 7, with the permission of AIP Publishing.

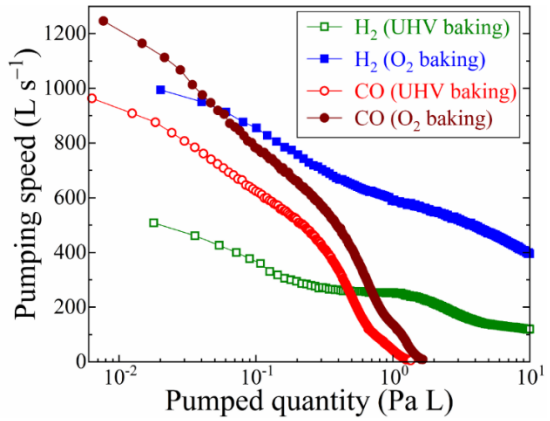

Fig. 7: Measured pumping speeds of the oxygen-free Pd/Ti coated chamber for H_2 or CO after UHV or O_2 baking at 150 °C for 12 hours. The apparatus used is shown in Fig. 1c. Reproduced from Ref. 7, with the permission of AIP Publishing.

Acknowledgement

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