MORPHOLOGIES OF OXYGEN-FREE TITANIUM AND PALLADIUM/TITANIUM THIN FILMS: NEW NON-EVAPORABLE GETTER (NEG) COATINGS

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Abstract

Non-evaporable getter (NEG) coatings are ideal for maintaining an ultrahigh vacuum (UHV) in the range 10^{-8} Pa and they are widely used for accelerators because they are oil free, magnetic-field free, vibration free, economical, space saving, and energy efficient. We recently fabricated new NEG coatings consisting of low-oxygen-content Ti or oxygen-free Pd/Ti by sublimation under a clean UHV in the range 10^{-8} to 10^{-7} Pa. Here, we report the determination of the morphologies of these films by scanning electron microscopy, transmission electron microscopy, scanning transmission electron microscopy, and energy-dispersive X-ray spectroscopy. The Ti and Pd films had almost uniform thicknesses of about 1.3 μm and 50 nm, respectively, and the Pd film completely overcoated the Ti film. Both the Pd and Ti thin films were uniformly deposited in plane on the stainless steel 304L substrate and they had polycrystalline structures. The interface between the Pd and Ti thin films was not abrupt.

INTRODUCTION

A non-evaporable getter (NEG) is a material, such as Al, Ti, V, Zr, Hf, Ta, Nb, Fe, or their alloys, that can evacuate reactive residual gases after activation under a clean ultrahigh vacuum (UHV) [1–3]. The NEG coating technique involves coating the inner walls of a vacuum chamber with thin film of a NEG material [4–6] and it is widely used in accelerators for synchrotron radiation facilities, because NEG thin films suppress outgassing from substrates and pump reactive residual gases, and because they are space saving. The most popular NEG coating consists of Ti, Zr, and V, deposited by dc magnetron sputtering; this technique was developed by Benvenuti *et al.* [4,5]. The resulting TiZrV thin film can be fully activated by baking at 180 °C for 24 hours. Recently, thin films of TiZrHfV deposited by dc magnetron sputtering have been reported to be fully activated by baking at 150–160 °C for 24 hours [6].

We recently developed a new NEG coating, and named it as oxygen-free Pd/Ti coating, principally for pumping H_2 and CO [7,8]. The oxygen-free Pd/Ti coating has the following advantages: (1) it can be activated after baking

at 133 °C for 12 hours; (2) the Pd overcoat prevents oxidation of the Ti film, even after repeated venting–baking cycles; (3) the initial and running costs are low; (4) its fabrication does not require skilled technicians; (5) it can be applied to chambers having a complex structure; and (6) it can be applied to narrow tubes, where Pd and Ti filaments can be arranged.

To produce this coating, a thin film of Ti is initially deposited and subsequently overcoated with Pd under clean UHV conditions in the range 10^{-8} to 10^{-7} Pa. The activation and pumping processes for the oxygen-free Pd/Ti thin film differ from those used for conventional NEG coatings [9]. In the activation process of conventional NEG, C and O atoms chemisorbed on the NEG surface diffuse into the bulk to provide a clean and reactive surface [3]. Consequently, the activation temperature of conventional NEG films is determined mainly by the diffusion activation energies of C and O atoms. On the other hand, the oxygen-free Pd/Ti thin film is activated by the diffusion of H atoms from the Ti film through the Pd overcoating to the surface, where they desorb into the vacuum as H_2 molecules. The activation energies for surface adsorption and bulk dissolution of H are −0.53 and −0.1 eV, respectively, for Pd, and −0.92 and −0.47 eV, respectively, for Ti [10]. During this activation process, CO chemisorbed on the Pd surface is also desorbed, leaving the surface available for CO absorption [11]. Because the activation temperature of oxygen-free Pd/Ti thin film is determined by the diffusion and desorption energies of hydrogen as well by the desorption energy of CO, the activation temperature can be reduced to as low as 133 °C [7,8]. When an ionization gauge is used in a vacuum system, oxygen-free Pd/Ti is expected to pump hydrogen-containing molecules, such as H_2O or CH_4, because electrons emitted from the gauge dissociates these molecules into H atoms and radicals such as O and C.

Here, we report the morphologies of the low-oxygen-content Ti and oxygen-free Pd/Ti thin films as determined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy (EDS).

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EXPERIMENTAL METHODS

The apparatus that we used for the preparation of low-oxygen-content Ti and oxygen-free Pd/Ti samples for SEM, TEM, STEM, and EDS observations is described elsewhere [9]. The oxygen-free Pd/Ti film was deposited on a substrate of electropolished stainless steel 304L (SS304L) by the following procedure. An UHV chamber was baked for 12 hours at 150 °C, then cooled to room temperature. A Ti filament was sublimed at 50 A for 333 minutes under a pressure of 2.2×10^{-7} Pa. Next, a Pd filament was sublimed at 22 A for 111 minutes at a pressure of 1.8×10^{-8} Pa. Low-oxygen content Ti samples were similarly prepared, but without deposition of Pd. The concentration of oxygen in the Pd/Ti film and the Ti bulk was estimated to be less than 0.05% [7].

Sample observations were carried out at the National Institute of Material Science (NIMS) TEM station. SEM observations were carried out by using JSM-7000F instrument (JEOL Ltd., Tokyo) operated at an accelerating voltage of 15 kV. TEM observations were carried out by using a JEM-2100F microscope (JEOL) operated at an accelerating voltage of 200 kV.

RESULTS

Figure 1a shows an SEM image of the cross section of the low-oxygen-content Ti thin film. This had a uniform thickness and a columnar structure. Figures 1b and 1c show SEM images of the surface of the Ti thin film, which had a scale-shaped structure. The grooves observed on the Ti surface derive from those present on the SS304L substrate. X-ray photoelectron spectroscopy (XPS) has shown that the Ti surface oxidizes when it is exposed to the atmosphere [7].
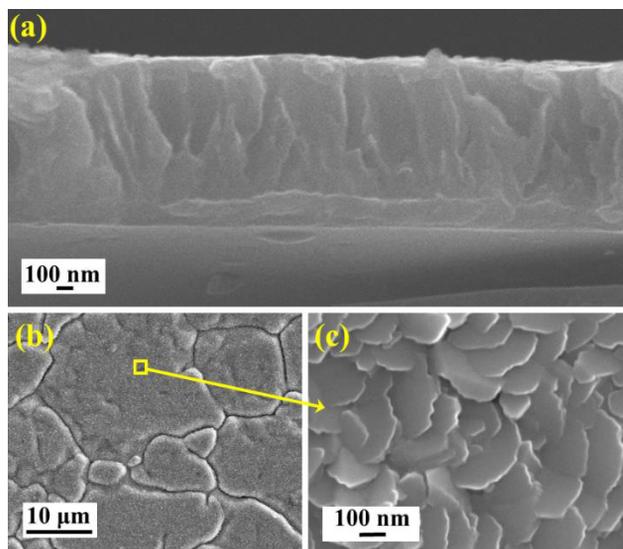
Figure 1: SEM images of (a) the cross section, (b) the surface, and (c) the enlarged surface of the low-oxygen-content Ti thin film.

Figures 2a and 2b show SEM images of the surface of the oxygen-free Pd/Ti thin film. The surface has an uneven structure with irregularities of several tens to several hundreds of nanometers, as shown in Fig. 2b. Figures 2c and 2d show the EDS elemental maps for Pd and Ti, respectively, in the same region as Fig. 2a. The fluorescence X-rays of Pd and Ti were both uniformly mapped, indicating that the Pd and Ti thin films were uniformly deposited in plane on the SS304L substrate. Because the depth resolution of EDS is approximately 1 μm, fluorescence X-rays from the Ti thin film under the Pd thin film were also detected. The SEM image of the cross section of the oxygen-free Pd/Ti film was similar to that shown in Fig. 1a [7].
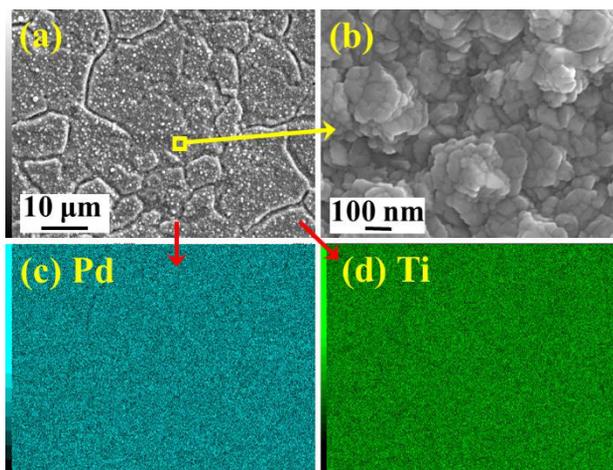
Figure 2: SEM images of (a) the surface, and (b) the enlarged surface of the oxygen-free Pd/Ti thin film. The EDS elemental maps of (c) Pd, and (d) Ti show the same region as (a).

Figures 3a and 3d show TEM bright-field images of the cross sections of the Pd and Ti thin films, respectively, whereas Figs. 3b and 3e show fast-Fourier-transform (FFT) patterns of Figs. 3a and 3d, respectively. These images indicate that the Pd and Ti thin films have polycrystalline structures. Figures 3c and 3f show TEM images of the cross sections of the interfaces between the Pd and Ti thin films, and between the Ti thin film and the SS304L substrate, respectively. The interface between the Pd and Ti thin films was not abrupt, whereas the interface between the Ti film and SS304L substrate was abrupt. At the interface, atomic layers with an atomic weight smaller than that of Ti were observed, as shown in Fig. 3f, suggesting that Cr_2O_3 segregates to the SS304L surface [12]. XPS measurements have shown that the Pd surface does not oxidize, even when it is exposed to the atmosphere [7].
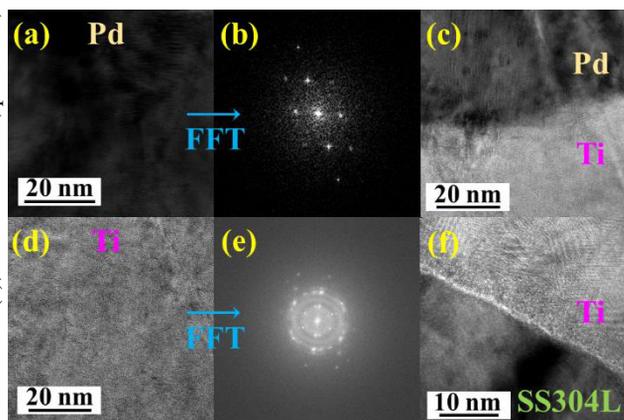
Figure 3: TEM bright-field images of cross sections of (a) Pd and (d) Ti thin films of the oxygen-free Pd/Ti thin film. Fast-Fourier-transform images of cross section of (b) the Pd and (e) Ti thin films. TEM images of cross sections of (c) the interface between the Pd and Ti thin films, and (f) the interface between the Ti thin film and SS304L substrate.

Figures 4a and 4b show STEM dark-field images of a cross section of the oxygen-free Pd/Ti thin film, prepared by focus ion milling. Figures 4c and 4d show EDS elemental maps of Pd and Ti, respectively, in the same region as Fig. 4b. These results show that the Ti and Pd films have an almost uniform thickness of approximately 1.3 µm and 50 nm, respectively, and that the Pd film completely overcoats the Ti film.
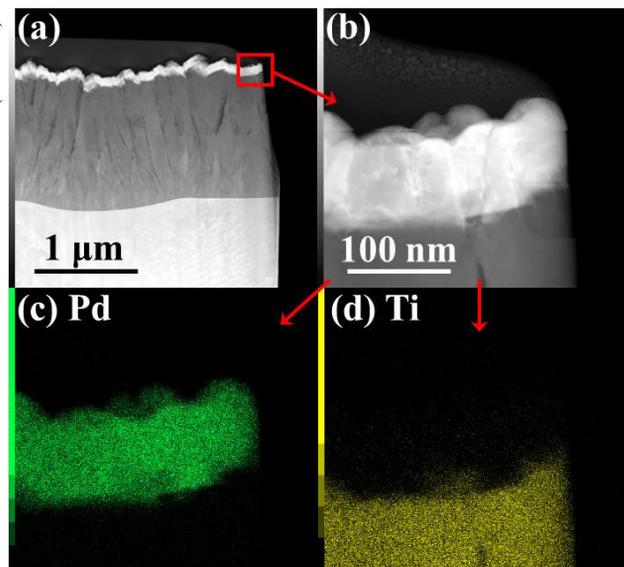
Figure 4: (a) STEM and (b) enlarged STEM dark-field images of the cross section of the oxygen-free Pd/Ti thin film. EDS images of (c) Pd and (d) Ti in the same region as (b).

Figures 5a and 5b show STEM dark-field images of cross section of the oxygen-free Pd/Ti thin film. Figures

5c, 5d, 5e, and 5f show EDS elemental maps for Ti, Fe, Cr, and Ni, respectively in the same region as Fig. 5b. At the interface between the Ti and SS304L, atomic layers with a smaller atomic weight than that of Ti were observed. The elemental map of Cr was slightly thicker than those of Fe and Ni, as shown in Figs 5d, 5e, and 5f. These results also support that Cr_2O_3 segregates on the SS304L surface [12].
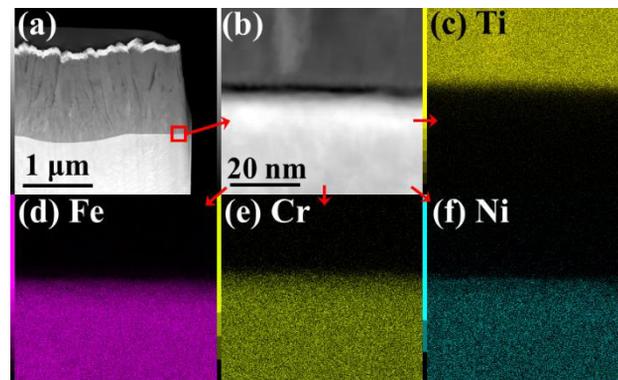
Figure 5: (a) STEM and (b) enlarged STEM dark-field images of a cross section of the oxygen-free Pd/Ti thin film. EDS images of (c) Ti, (d) Fe, (e) Cr, and (f) Ni in the same region as (b).

CONCLUSIONS

The morphologies of low-oxygen-content Ti and oxygen-free Pd/Ti films were examined by SEM, TEM, STEM, and EDS. The Ti and Pd films had almost uniform thicknesses of approximately 1.3 µm and 50 nm, respectively, and the Pd film completely overcoated the Ti film. Both the Pd and Ti thin films were uniformly deposited in plane on the SS304L substrate and had polycrystalline structures. The interface between the Pd and Ti thin films was not abrupt.

ACKNOWLEDGMENTS

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