STUDY ON THE VACUUM PROPERTIES OF Pd/Ti BILAYER THIN FILM*

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Abstract

Non-evaporable getter (NEG) thin films are essential for achieving ultra-high vacuum in the narrow-bore chambers. Pd/Ti bilayer NEG thin films were deposited on oxygen-free copper and silicon substrates by DC magnetron sputtering. The microstructure and elemental distribution were characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The films exhibit a cauliflower-like surface morphology and a columnar cross-sectional structure, providing a high specific surface area and effective pathways for gas diffusion. The pumping speed for H_2 was evaluated using the constant-pressure dynamic flow method after activation at 150 °C for 12 h. The pumping speed decreases from 0.13 to 0.02 L s^{-1} within a pumped quantity range of 1×10^{-5} - 6.5×10^{-3} Pa L. A non-monotonic variation in pumping speed was observed, which is attributed to hydrogen adsorption, dissociation on the Pd surface, and subsequent diffusion into the Ti layer for hydride formation. The results demonstrate that the Pd overlayer effectively enables low-temperature activation and enhances hydrogen sorption behavior, indicating that Pd/Ti NEG thin films are promising candidates for ultra-high vacuum applications in accelerator systems.

INTRODUCTION

The fourth-generation synchrotron radiation storage rings employ a Multi-Bend Achromat (MBA) lattice to achieve ultra-low emittance and ultra-high brightness, which are commonly referred to as diffraction-limited storage rings (DLSRs) [1]. This design necessitates small magnetic apertures and narrow-bore vacuum chambers integrated within the magnets. Conventional lumped pumping schemes are insufficient to provide the ultra-high vacuum (UHV) required for stable beam operation. To meet these UHV requirements, non-evaporable getter (NEG) thin films are typically deposited on the inner surfaces of the vacuum chambers [2]. NEG films can effectively suppress thermal outgassing from the chamber walls while simultaneously pumping residual gases without occupying additional space. Furthermore, NEG films exhibit low photon-stimulated desorption (PSD), low electron-stimulated desorption (ESD), and low secondary electron yield (SEY) [3, 4]. Since its development at CERN [5], NEG thin film technology has been widely adopted in particle accelerators, including LHC, ESRF, MAX IV, Diamond, and HEPS.

Activated NEG films exhibit strong physical and chemical sorption capabilities, effectively capturing reactive gases such as H_2, CO, CO_2, and H_2O. However, upon exposure to air, the film surface readily oxidizes to form a passivation layer, resulting in the loss of pumping capacity. Activation is essential for restoring the sorption performance of NEG thin films and is typically achieved by annealing under high vacuum (HV) or UHV. This thermal treatment promotes the desorption of surface oxides and their diffusion into the bulk, thereby removing the passivation layer and regenerating active metallic surfaces [6].

Due to its excellent oxidation resistance, a palladium (Pd) overlayer can be deposited on titanium (Ti) films to suppress oxidation of the underlying layer, thereby enabling a reduced activation temperature for Pd/Ti NEG thin films. Pd/Ti films were deposited on copper and silicon substrates by magnetron sputtering. The microstructure of the films was characterized, and the H_2 pumping speed was evaluated after activation by baking at 150 °C.

EXPERIMENTAL PROCEDURES

Sample Preparation

Pd/Ti films were deposited on oxygen-free copper (OFC) substrates (20 mm × 20 mm × 1 mm) and silicon substrates (10 mm × 10 mm × 1 mm) by DC magnetron sputtering in an argon atmosphere. Prior to deposition, the OFC substrates were subjected to acid cleaning followed by ammonium citrate passivation, while the silicon substrates were ultrasonically cleaned in acetone. After cleaning, all substrates were dried with high-purity nitrogen gas. It should be noted that the substrates were selected based on the specific requirements of each characterization: OFC substrates were employed for the pumping speed measurements, whereas silicon substrates were utilized for the microstructure Characterization. High-purity Ti (99.99%) and Pd (99.95%) targets were used. The Ti target was sputtered at a current of 0.6 A for 4 h under a working pressure of 2 Pa, followed by Pd deposition at a current of 0.15 A for 5 min under the same pressure. During deposition, the Ti target was replaced by the Pd target in situ without breaking vacuum. The thicknesses of the Ti and Pd layers were approximately 433 nm and 56 nm, respectively. The main characteristics of the Ti and Pd/Ti films are summarized in Table 1.

Table 1: Deposition parameters for Pd/Ti thin films

Film	Working pressure [Pa]	Working current [A]	Working gas	Thickness [nm]
Ti	2	0.6	Ar	433
Pd	2	0.15	Ar	56

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Microstructure Characterization

The surface morphology and cross-sectional thickness of the films were characterized using a Gemini 500 scanning electron microscope (SEM). Energy-dispersive X-ray spectroscopy (EDS) attached to the SEM was used to analyze the elemental composition and distribution across the film cross-section.

Pumping Speed Measurement

The pumping speed of the Pd/Ti thin films for H_2 was measured using the constant-pressure dynamic flow method, as schematically shown in Fig. 1. The experimental setup primarily consisted of a sample chamber, a loading chamber, a calibrated orifice with known conductance, an injection chamber, vacuum valves, a pumping station, and high-precision vacuum gauges. To achieve UHV conditions, the loading and injection chambers were baked at 200°C for 48 h. The sample chamber was not baked during this stage; subsequently, the Pd/Ti films within the sample chamber were activated at 150°C for 12 h. After activation, the angle valves isolating the pumping system from the loading and injection chambers were closed. The test gas was then introduced into the injection chamber through a needle valve. During the measurement, the pressure in the loading chamber was maintained within the range of 1×10^{-4} Pa - 1×10^{-3} Pa as possible by continuously modulating the needle valve to ensure a steady-state pressure throughout the testing process.

The pumping speed S (L s^{-1}) of the getter thin film was calculated as:

$$S = C \cdot \frac{P_{inj} - P_{load}}{P_{load}} \tag{1}$$

where C is the conductance of the orifice, and P_{inj} and P_{load} are the pressures in the injection and loading chambers, respectively.

The cumulative amount of gas adsorbed by the getter film, $Q(t)$, was calculated as:

$$Q(t) = \int_0^t C[P_{inj}(t) - P_{load}(t)]dt \tag{2}$$

where $P_{inj}(t)$ and $P_{load}(t)$ are the time-dependent pressures in the injection and loading chambers, respectively.

RESULTS AND DISCUSSION

Surface and Cross-Section Morphologies

Figure 2(a) shows the surface morphology of the Pd/Ti film, which exhibits a cauliflower-like structure. The cross-sectional shape of the Pd/Ti film, as depicted in Fig. 2(b), exhibits a columnar structure, which provides effective pathways and storage sites for gas diffusion and adsorption. Compared with dense films, the columnar structure provides a higher specific surface area, which is beneficial for getter performance by enhancing gas adsorption and diffusion kinetics.

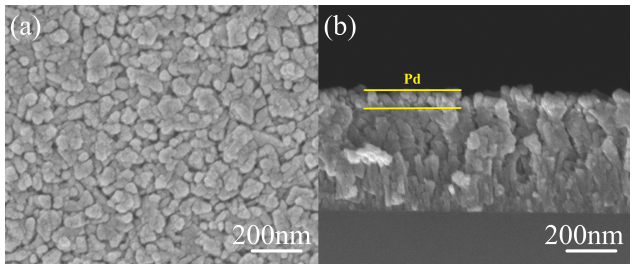

Figure 2: Surface (a) and cross-sectional (b) morphology SEM images of Pd/Ti film

Figure 3 shows the cross-sectional elemental distributions obtained by EDS, indicating that Pd is uniformly distributed in the top layer, while Ti dominates the underlying layer. This result confirms the successful formation of a Pd overlayer on the Ti film.

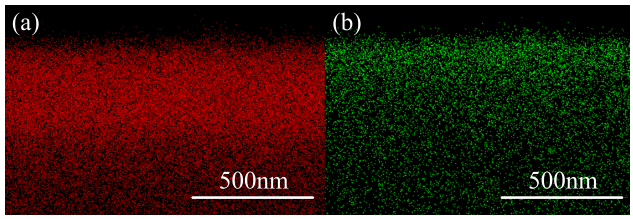

Figure 3: The cross-sectional EDS images of Pd/Ti film (a)Ti,(b)Pd

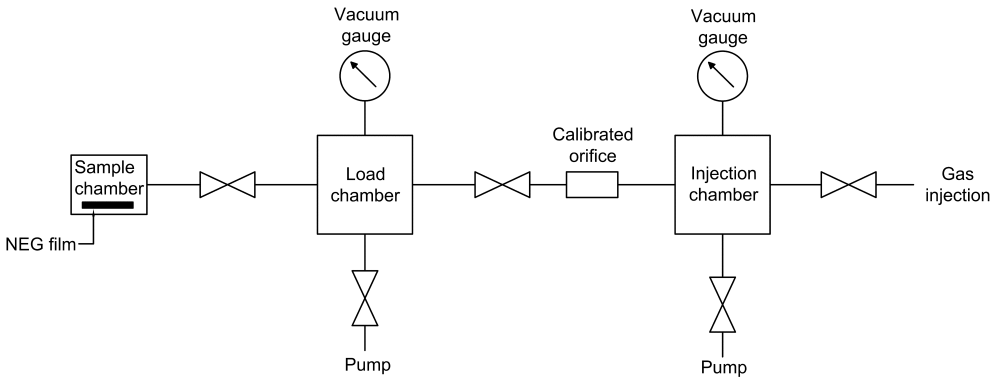

Figure 1: Schematic diagram of the pumping speed experimental setup based on the constant-pressure dynamic flow method.

Pumping Speed

Figure 4 shows the pumping speed of the Pd/Ti thin film for H_2 after activation at 150°C for 12 h. Within the pumped quantity range of 1×10^{-5} to 6.5×10^{-3} Pa L, the pumping speed ranges from decreases from 0.13 to 0.02 L s^{-1}.

At the initial stage of H_2 exposure, the pumping speed exhibits a sharp decrease to approximately 0.067 L s^{-1}, followed by a transient recovery to 0.076 L s^{-1},and subsequently decreases gradually to 0.02 L s^{-1}. This non-monotonic behavior is attributed to the hydrogen transport in the Pd/Ti bilayer structure [7]. After surface adsorption and dissociation on Pd, hydrogen atoms diffuse through the Pd overlayer and are absorbed by the Ti layer, where stable hydrides are formed.The initial decrease is associated with rapid surface coverage, while the subsequent increase suggests enhanced hydrogen diffusion into the Ti layer after activation of diffusion pathways through the Pd overlayer.

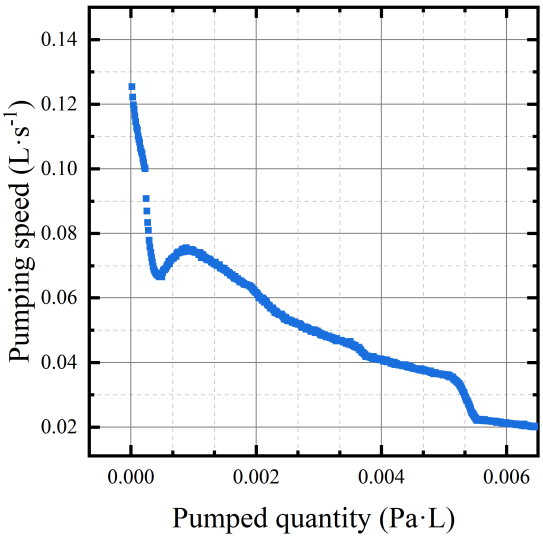

Figure 4: Pumping speed of the Pd/Ti film

CONCLUSION

Pd/Ti bilayer NEG thin films were successfully deposited by DC magnetron sputtering, and their microstructure and pumping speed for H_2 were investigated. The films exhibit a cauliflower-like surface morphology and a columnar cross-sectional structure, which provide an increased specific surface area and facilitate gas diffusion.After activation at a low temperature of 150 °C, the Pd/Ti films demonstrate effective pumping speed for H_2 , with a ranging from 0.13 to 0.02 L s^{-1} over the tested sorption range. The observed non-monotonic variation in pumping speed is attributed to the combined effects of hydrogen adsorption, dissociation on the Pd overlayer, and diffusion into the Ti layer for hydride formation.The introduction of the Pd overlayer effectively suppresses surface oxidation and promotes hydrogen transport, enabling low-temperature activation and improved getter performance. These findings highlight the potential of Pd/Ti NEG thin films for application in ultra-high vacuum environments, particularly in accelerator systems.

REFERENCES

[1] Z. B. Sun, L. Shang, F. L. Shang, Y. G. Tang, W. Liu, and W. B. Song, "Simulation study of longitudinal injection scheme for HALS with a higher harmonic cavity system", *Nucl. Sci. Tech.*, vol. 30, p. 113, 2019. doi:10.1007/s41365-019-0627-x

[2] C. Benvenuti, P. Chiggiato, F. Cicoira, and V. Ruzinov, "Nonevaporable getter films for ultrahigh vacuum applications", *J. Vac. Sci. Technol. A*, vol. 16, no. 1, pp. 148-154, 1998. doi:10.1116/1.580963

[3] P. Chiggiato and R. Kersevan, "Synchrotron radiation-induced desorption from a NEG-coated vacuum chamber", *Vacuum*, vol. 60, no. 1-2, pp. 67-72, 2001. doi:10.1016/S0042-207X(00)00247-5

[4] O. B. Malyshev, A. P. Smith, R. Valizadeh, and A. Valizadeh, "Electron stimulated desorption from bare and nonevaporable getter coated stainless steels", *J. Vac. Sci. Technol. A*, vol. 28, no. 6, pp. 1215-1225, 2010. doi:10.1116/1.3478672

[5] C. Benvenuti, P. Chiggiato, P. Costa Pinto *et al.*, "Vacuum properties of TiZrV non-evaporable getter films", *Vacuum*, vol. 60, no. 1-2, pp. 57-65, 2001. doi:10.1016/S0042-207X(00)00246-3

[6] S. H. Wang, Z. W. Wang, X. Shu, W. Wei, Y. H. Gao, and Y. Wang, "Activation characterization of Ti–Zr–V getter films deposited by magnetron sputtering", *Appl. Surf. Sci.*, vol. 528, p. 147059, 2020. doi:10.1016/j.apsusc.2020.147059

[7] M. Matsumoto, T. Okada, T. Miyazawa, K. Mase, M. Yamanaka, A. Hashimoto, M. Wilde, and K. Fukutani, "Hydrogen incorporation and release from nonevaporable getter coatings based on oxygen-free Pd/Ti thin films", *J. Vac. Sci. Technol. A*, vol. 37, no. 5, p. 051601, 2019. doi:10.1116/1.5108983