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OXYGEN-FREE TITANIUM THIN FILM AS A NEW NONEVAPORABLE GETTER WITH AN ACTIVATION TEMPERATURE AS LOW AS 185 °C

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Abstract

Although nonevaporable getter (NEG) pumps are widely used in synchrotron-radiation facilities, unalloyed titanium (Ti) has rarely been used as a NEG. It has been previously shown that high-purity Ti deposited under an ultrahigh vacuum, followed by introduction of N_2, operated as a NEG with an activation temperature of 185 °C. This Ti thin film contained a concentration of oxygen and related impurities of 0.05% or less. In the present study, we used synchrotron-radiation X-ray photoelectron spectroscopy to analyze the oxygen-free Ti thin films after the introduction of high-purity N_2 or air. After the deposition of oxygen-free Ti, more surface TiN was formed by the introduction of high-purity N_2 than by introduction of air. We also evaluated the pumping properties of the oxygen-free Ti thin films treated with high-purity N_2 by means of total and partial pressure measurements. A vacuum vessel with oxygen-free Ti deposited on its inner walls was found to pump H_2, H_2O, O_2, and CO even after 30 cycles of pumping, baking at 185 °C for 6 hours, cooling to room temperature, introduction of high-purity N_2, and exposure to air. The high purity of the Ti thin film and the formation of TiN on its surface appear to be responsible for the reduced activation temperature of 185 °C.

INTRODUCTION

A nonevaporable getter (NEG) is a material that evacuates residual reactive gases at room temperature after it has been activated under clean ultrahigh-vacuum (UHV) conditions (Fig. 1) [1–3]. In 1997, Benvenuti *et al.* proposed the idea of depositing NEG thin films on the inner walls of vacuum chambers to achieve an UHV after baking [4–6]. They named this method 'NEG coating'. Soon afterward, they reported that thin films of TiZrV deposited by direct-current magnetron sputtering can be activated by baking at 180–250 °C for 24 hours [7, 8]. This TiZrV coating was used with great success at the European Organization for Nuclear Research (CERN) and has now been adopted in accelerator facilities around the world [9, 10].

Although a single-metal Ti deposition is widely used in Ti sublimation pumps [11], it has rarely been used as a NEG coating because its activation temperature has been reported to be as high as 350–400 °C [4–6]. However, Miyazawa *et al.* found that a thin film of high-purity Ti deposited by sublimation of Ti metal under UHV followed by introduction of N_2 can work as a NEG with an activation temperature of 185 °C [12, 13]. Because the concentration of oxygen and related impurities in the Ti thin film was 0.05% or less, we refer to it as 'oxygen-free Ti' hereafter. Here, we present the results of our study by synchrotron-radiation X-ray photoelectron spectroscopy (SR-XPS) of oxygen-free Ti thin films treated with high-purity N_2, together with measurements of total and partial pressures to verify their NEG properties [14].

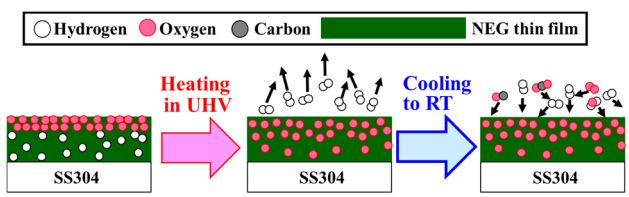

Figure 1: Schematic showing the activation and pumping mechanisms of a NEG thin film deposited on an SS304 stainless-steel substrate.

EXPERIMENTS

Thin films of oxygen-free Ti were deposited on silicon wafers or the inner surfaces of a vacuum vessel by means of Ti sublimation under UHV in the range 10^{-7} to 10^{-8} Pa. N_2 with a purity of more than 99.9% was then introduced (Figs. 2-4). The purity of the oxygen-free Ti thin films was estimated to be more than 99.995% from the pressure and the Ti deposition rate. The oxygen-free Ti thin films were analyzed by SR-XPS at BL-13B of the Photon Factory

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[15]. The total-pressure curves and mass spectra of residual gases in the vacuum vessel were measured by using the apparatus shown in Fig. 5. The procedure for repeatedly measuring the total pressure curves and the mass spectra of residual gases is outlined in Fig. 6.

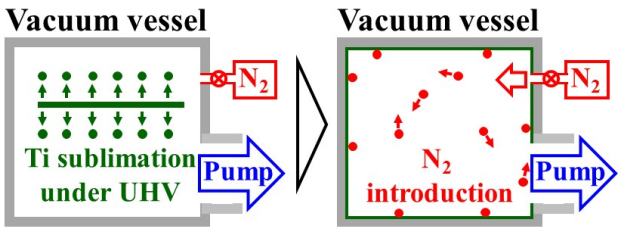

Figure 2: Schematic showing the procedure for deposition of the oxygen-free Ti thin film followed by introduction of high-purity N_2.

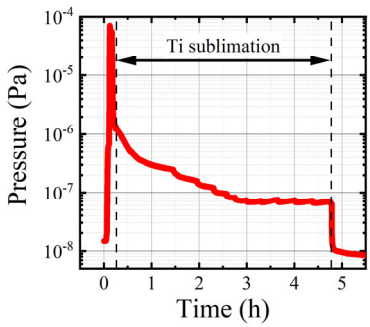

Figure 3: Total pressure curve in the chamber during deposition of the oxygen-free Ti thin film.

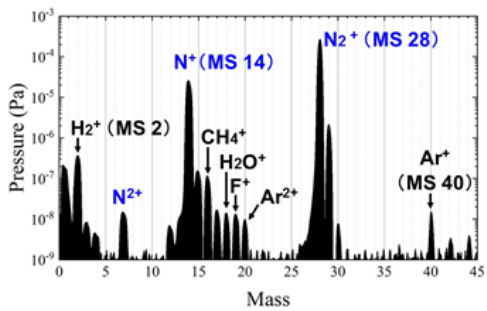

Figure 4: Mass spectrum of introduced high-purity N_2. The quadrupole mass spectrometer used was uncalibrated.

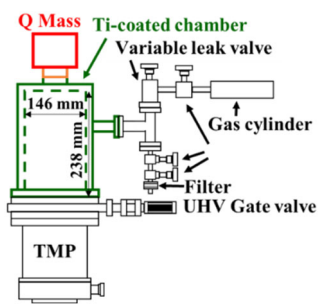

Figure 5: Apparatus for measurements of the total and partial pressures, and mass spectra of residual gases.

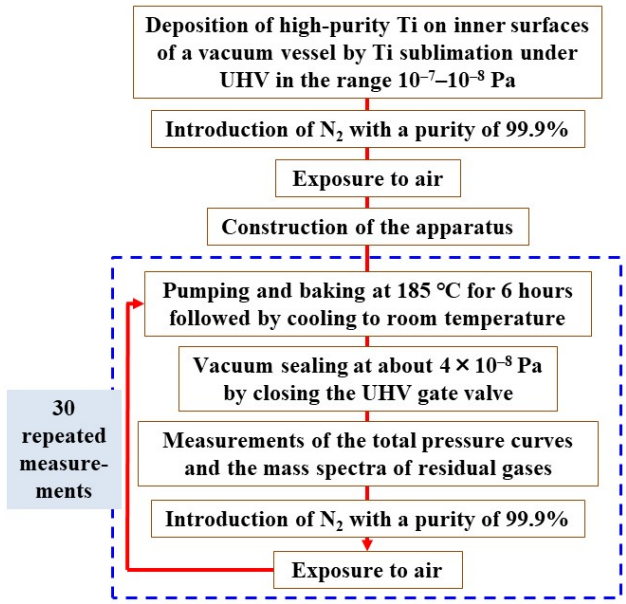

Figure 6: The procedure for 30 repeated measurements of the total pressure curves and the mass spectra of residual gases.

SR-XPS SPECTRA

SR-XPS spectra in the N 1s core-level region showed that the N 1s peaks consisted of multiple components from nitride species (396.6 eV) and adsorbates with nitrogen-containing functional groups, such as cyanides or anilines (399 eV) or nitroxides (400.5 eV) (Fig. 7). The greater height of the nitride peak of the oxygen-free Ti film after introduction of high-purity N_2 (N_2 vent) was much higher than that of the air-introduced sample (air vent), showing that the surface of the N_2 vent sample surface was nitrided to a greater extent than the air vent sample [14]. Wide-scan, Ti 2p region, and O 1s region SR-XPS spectra were almost identical for the N_2 vent and air vent samples [14]. These results showed that the surfaces of the oxygen-free Ti thin films were highly nitrided when high-purity N_2 was introduced before exposure to air, whereas they were less nitrided when air was introduced first.

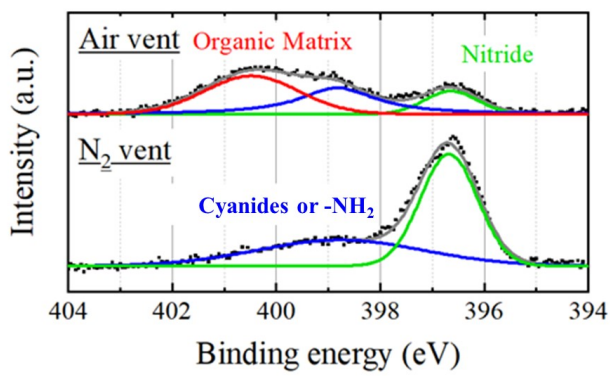

Figure 7: Enlarged SR-XPS spectra in the region of N 1s peaks. Reproduced from Ref. 14, with the permission of Particle Accelerator Society of Japan (PASJ).

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TOTAL PRESSURE CURVES AND MASS SPECTRA

Figure 8 shows total-pressure curves for a vessel coated with oxygen-free Ti as a function of the number of cycles of pumping, baking at 185 °C for 6 hours, cooling to room temperature (RT), closure of the UHV gate valve, introduction of high-purity N_2, and exposure to air. The pressures in the oxygen-free Ti coated vessel after closure of the UHV gate valve were found to be more than two orders of magnitude smaller than those in the uncoated vacuum vessel. Figure 9 shows total and partial pressure curves of the oxygen-free Ti coated vessel for the first cycle of pumping, baking at 185 °C for 6 hours, cooling to RT, and closure of the UHV gate valve. Figure 10 shows mass spectra of the residual gases after five hours of vacuum sealing of the vacuum vessel coated with oxygen-free Ti. The main components of the residual gas were Ar and CH_4. This result is reasonable because clean Ti thin films do not pump Ar or CH_4 [11]. Under vacuum

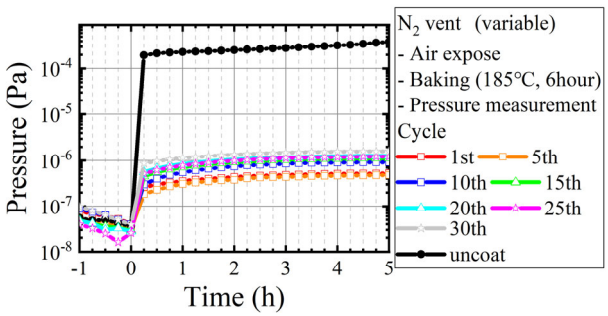

Figure 8: Total pressure curves of the oxygen-free Ti coated vessel as a function of cycles of pumping, baking at 185 °C for 6 hours, cooling to RT, closure of the UHV gate valve, introduction of high-purity N_2, and exposure to air. Reproduced from Ref. 14, with the permission of PASJ. The quadrupole mass spectrometer used was uncalibrated.

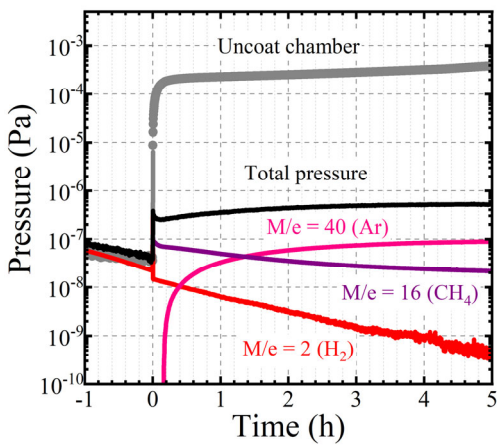

Figure 9: Total and partial pressure curves of the oxygen-free Ti coated vessel for the first cycle of pumping, baking at 185 °C for 6 hours, cooling to RT, and closure of the UHV gate valve. The quadrupole mass spectrometer used was uncalibrated.

sealing after 30 cycles of baking and exposure to air, the partial pressure of H_2 was less than 5×10^{-7} Pa, and the partial pressures of H_2O, O_2, and CO were all less than 1×10^{-8} Pa. These results show that the vacuum vessel onto which oxygen-free Ti was deposited and into which high-purity N_2 was introduced continued to evacuate various reactive residual gases, such as H_2O, H_2, O_2, and CO, even after 30 cycles of baking and exposure to air.

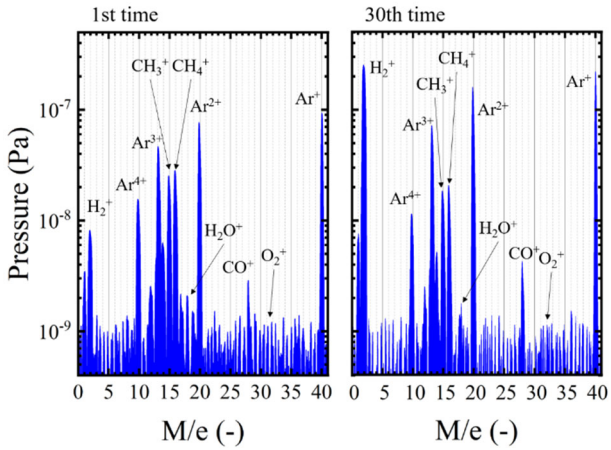

Figure 10: Mass spectra of residual gases after 5 hours of vacuum sealing of the oxygen-free Ti coated vessel for the first and 30th cycles of pumping, baking at 185 °C for 6 hours, cooling to RT, closure of the UHV gate valve, introduction of high-purity N_2, and exposure to air. The quadrupole mass spectrometer used was uncalibrated.

CONCLUSION

The SR-XPS spectra showed that the surfaces of the oxygen-free Ti thin films were highly nitrided when high-purity N_2 was introduced before exposure to air, whereas they were less nitrided when air was introduced first. Furthermore, the vacuum vessel onto which oxygen-free Ti was deposited and high-purity N_2 was introduced was found to evacuate H_2O, H_2, O_2, and CO, even after 30 cycles of pumping, baking and exposure to air. This oxygen-free Ti deposition technology can be applied to accelerators, beamlines, or endstations in SR facilities. The high purity of the Ti thin film and the formation of TiN on its surface appear to be responsible for the reduced activation temperature, which is as low as 185 °C.

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