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Surface characterization of activated Ti–Zr–V NEG coatings

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ABSTRACT

The thermally activated Ti–Zr–V non-evaporable getter (NEG) film has been studied by means of X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS). Depth profiling technique has been used to establish the location of different components in the near-surface region. It was found that the top surface layer of the activated Ti–Zr–V NEG film is zirconium and titanium enriched. Residual oxide observed even on fully activated NEG surface consists mostly of zirconium and titanium low valence suboxides that are located mainly in the top surface layer. Carbides formed during the activation process remain on the surface and their concentration drops strongly with depth.

1. Introduction

Non-evaporable getters (NEGs) are used as active pumping systems permitting the achievement of ultra-high vacuum of the order 10^{-11} mbar and lower. NEGs are well suited for efficient pumping of low aperture vacuum devices due to their distributed pumping action [1–6]. An especially important application of NEGs is the achievement of low ultimate pressures in collider facilities [1,7,8].

Lowering of the activation temperature is an important way to extend the range of NEGs' practical use. Ti–Zr–V non-evaporable getter coatings developed at CERN have been found to exhibit an activation temperature below 200 °C [9,10]. Features provided by Ti–Zr–V coatings make them attractive for a variety of R&D applications. Nevertheless, mechanisms involved in their thermal activation and pumping action are not fully explained yet. Understanding of these processes is essential to further development of NEG coatings.

It has been previously reported [11–13] that during the activation process surface oxides covering air exposed Ti–Zr–V NEG are reduced, oxygen is dissolved in the bulk and carbon is converted to carbides. Studies of Ti–Zr–V coatings of various compositions [14] showed that binary Zr–V NEGs exhibit similar properties as ternary ones. Relative simplicity of Zr–V binaries has been found advantageous to get insight into activation and gettering mechanisms. Therefore several studies [15–19] have been devoted to the investigation of Zr–V NEGs by means of surface sensitive techniques, as gettering properties are first of all related to the getter surface characteristics. Depth resolved studies [16,19] showed the different surface composition of the activated Zr–V NEG relative to the bulk. The surface of activated Zr–V NEG coating is zirconium enriched, residual suboxides are observed mainly in the top surface layers and carbides formed during thermal activation are located in the subsurface region.

In this paper, we report an X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS) depth profiling study concerned with the surface characteristics of the activated Ti–Zr–V NEG coating.

2. Experiment

The thin film Ti–Zr–V getter was deposited by DC magnetron sputtering technique on a stainless-steel substrate (1×1 cm^2) at ambient temperature in an argon atmosphere (Ar pressure of 0.8 Pa, Ar^+ ion current density 3 mA/cm^2, high voltage about 520 V, deposition time 25 min, thickness approximately 1 μm). This procedure produces compact Ti–Zr–V coating with smooth surface [10]. The composition of the coating assessed by XPS quantitative analysis is $Ti_{25}Zr_{50}V_{25}$.

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The XPS and LEIS experiments were performed using Specs Phoibos 150 multichannel hemispherical analyzer with Mg K_α line (1253.6 eV) and He^+ (2 keV) beam as incident radiation, respectively. The base pressure in the UHV experimental chamber was around 1×10^{-10} mbar.

The thin film Ti–Zr–V NEG was activated at first by heating at 200 °C for 20 h and the activated NEG surface was then sputtered by Ar^+ ions. Surface analysis was performed in several phases of the sample treatment.

3. Results and discussion

Two approaches were chosen to establish the location of the different components in the near-surface region of activated Ti–Zr–V NEG film. XPS depth profiling was combined with acquisition of XPS spectra of photoelectrons emitted at 0° (normal to the sample surface) and 60° to obtain additional depth resolved data and to eliminate possible perturbing effects of Ar^+ ion sputtering.

Ti 2p, Zr 3d, V 2p, O 1s and C 1s photoelectron spectra were recorded during thermal activation and during following Ar^+ ion sputtering performed in several steps (1 keV, 2 μA/cm^2, total sputtering time 2 h). Selected XPS spectra are plotted in Fig. 1a–e.

Air exposed (as received) NEG surface is covered by oxide layer. It is illustrated in Fig. 1a by Ti^{4+} $2p_{3/2}$ $2p_{1/2}$ spin-orbit doublet at the binding energy ($2p_{3/2}$ BE) of 458.7 eV and in Fig. 1b by Zr^{4+} $3d_{5/2}$ $3d_{3/2}$ doublet at BE 182.3 eV ($3d_{5/2}$) characteristic for stoichiometric TiO_2 [20] and ZrO_2 [21], respectively. V $2p_{3/2}$ spectrum of air exposed NEG in Fig. 1c exhibits a broad peak which can be decomposed in several V^{n+} states [22] representing a mixed valence vanadium oxide. The different shape of V $2p_{3/2}$ spectrum of air exposed NEG taken at emission angle 60° in comparison with the normal emission one (Fig. 1c – bottom) indicates a variation of vanadium oxide stoichiometry depending on depth. In contrast with the Zr–V studies [15,16], synthetic components model of V $2p_{3/2}$ spectra exhibited no V^{5+} contribution. The O 1s spectrum of air exposed NEG film (Fig. 1d) shows main contribution around BE 530.2 eV corresponding to a metal oxide and a shoulder on the high BE edge (well pronounced mainly at 60° emission angle) attributed to oxygen containing adsorbates [23]. The multicomponent C 1s spectrum of the air exposed NEG in Fig. 1e represents the surface carbon and carbon containing adsorbates.

Reduction of the NEG surface during thermal activation is reflected by an attenuated O 1s peak intensity (Fig. 1d) and by an appearance of metallic Ti^0 (BE 454.0 eV), Zr^0 (BE 178.9 eV) and V^0 (BE 512.2 eV) [24] as can be seen in the spectra of activated Ti–Zr–V NEG film. Shape differences of Ti 2p, Zr 3d and V $2p_{3/2}$ spectra for photoemission angles 0° and 60° indicate the presence of suboxidic and/or carbidic contributions. The C1s spectra of activated NEG surface show a single peak at BE 281.9 eV characteristic for carbide [24].

Subsequent Ar^+ ion sputtering of the activated NEG led to a decrease of O 1s and C 1s peak intensities. Decreasing oxides and carbides concentrations are reflected by a low contribution of oxidic and/or carbidic species in Ti 2p, Zr 3d and V $2p_{3/2}$ spectra of ion sputtered NEG surface giving them a nearly metallic character.

The evolution of Ti 2p, Zr 3d, V $2p_{3/2}$, O 1s and C 1s intensities (normal emission) during the sample treatment is shown in Fig. 2. During the thermal activation, a decrease of O 1s and C 1s intensities followed by their stagnancy was observed. It illustrates the desorption of carbon and oxygen containing adsorbates together with the fast reduction of surface oxides at the beginning of the thermal activation process. Depth profiles during Ar^+ ion sputtering then show decreasing Ti 2p, Zr 3d, O 1s and C 1s intensities and increasing V $2p_{3/2}$ intensity. It suggests that the top surface layer is enriched with titanium and zirconium, as well as suboxidic and carbidic species.

The comparison of XPS intensity ratios of 0° (normal) and 60° photoemission angles for the activated and ion sputtered Ti–Zr–V NEG is shown in Fig. 3. M^{ox} (metal-oxide intensity – sum of all suboxidic contributions) and M^m (metallic state intensity) were

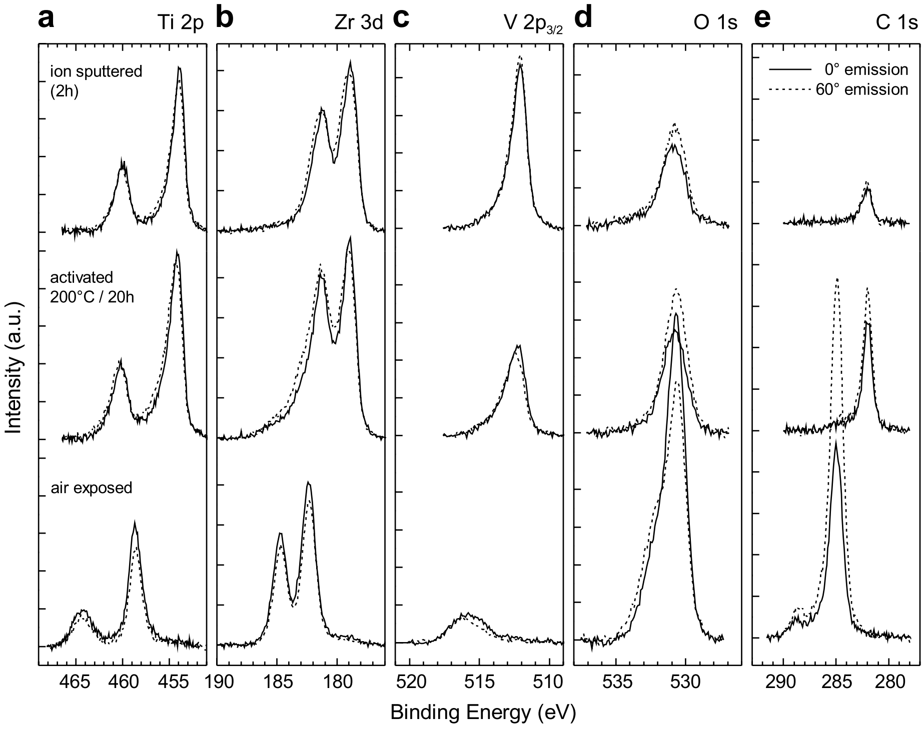

Fig. 1. Selected (a) Ti 2p, (b) Zr 3d, (c) V $2p_{3/2}$, (d) O 1s and (e) C 1s XPS spectra recorded at 0° (normal; solid lines) and 60° (dashed lines) emission angles illustrating evolution of Ti–Zr–V NEG surface during sample treatment (thermal activation and Ar^+ ion sputtering).