Ti–Zr–V Thin Films as Non-Evaporable Getters (NEG) to Produce Extreme High Vacuum

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Abstract: Non-evaporable getter (NEG) materials have become an integral part of many ultrahigh vacuum environments mainly due to their unique surface properties which are conducive to achieving extreme-high vacuum conditions of the order of $10^{-12}$ mbar and lower. These unique surface properties that lead to the gettering process can be found in pure metals as well as binary, ternary and multicomponent alloys from IV and V group elements of the periodic table. In this paper, we describe target preparation in alloy forms using pure titanium, zirconium and vanadium metals and preparation of Ti–Zr–V NEG thin films by a vacuum arc evaporation technique. The getter activation mechanism was investigated extensively by heat-treating the films under UHV conditions and characterizing using an in-situ XPS technique. The measurements of the activated getter films show the disappearance of the superficial oxide layer through the variation in the oxygen stoichiometry during thermal activation. The lowest activation temperature of about 160°C for a 2h heat-treatment was achieved with these films. Results of these studies show that the deposited films of Ti-Zr-V could be used as NEG to produce extreme high vacuum.

1. Introduction
It is obvious that surface outgassing is the main obstacle to achieve ultrahigh vacuum (UHV) conditions in all-metal vacuum systems. Physisorbed water molecules can be removed by continuous baking, yet in the presence of surface bombardment by electrons, ions, energetic neutrals, and synchrotron radiations clean metal surfaces are a steady source of gas, namely, H₂, CO, CO₂ and CH₄. As in modern UHV technology, continuous efforts have been done to reduce surface outgassing. Thin film coatings have been proposed as a path to reduce both thermal and bombardment induced degassing.

Non-evaporable getters (NEG) are utilized for efficient pumping of both low-aperture and sealed-off vacuum devices [1-3]. These can be made an integral part of any ultra high vacuum environments due to their unique surface properties and actively take part to achieve extreme high vacuum conditions of the orders of $10^{-12}$ mbar and lower. These unique surface characteristics based on gettering action can be found in pure metals as well as binary, ternary and multi-component alloys showing different behaviors depending on the type of alloying elements. Specifically, IV and V group
elements of the periodic table show the remarkable properties to perform as an active getter material. An important application of NEG’s is reduction of ultimate pressures in particle accelerators [1, 4-7]. NEG must be heated to up to the activation temperature $T_A$, the most important parameters for the field of NEG’s use.

Several studies have been conducted in the recent past utilizing thin films of Zr, either in pure form or in alloy form with titanium and vanadium to understand the gettering properties and the activation process [7, 8]. Different compositions of getter elements have been proposed to obtain lowest activation temperatures, Zr–V binaries and Ti–Zr–V ternaries have been found to exhibit activation temp. 200°C [9]. This is a surface phenomenon, many surface sensitive techniques such as Auger electron Spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) and Scanning tunneling microscope (SEM). In this paper, we are describe target preparation in alloy forms using pure titanium, zirconium and vanadium metals, preparation of Ti–Zr–V NEG thin films by a vacuum arc evaporation technique and results of characterization using an in-situ XPS technique for film thermally treated under UHV conditions at different temperatures to understand the activation mechanism.

2. Selection of Getter materials

During the activation of a NEG coated on stainless steel, oxides present on the surface are dissolved in the material bulk by heating. A low activation temperature implies high oxygen diffusivity in the getter film. To cope with the maximum baking temperature allowed by the mechanical properties of construction materials, activation should be feasible at temperatures not higher than 400°C for stainless steel or never higher than 200°C for vacuum chambers made of copper or aluminum alloys. On the other hand, the activation temperature should not be lower than 100–150°C to ensure stability in air at ambient temperature and to avoid water vapor pumping during the bakeout process. In both cases, the getter film would otherwise be unduly loaded with oxygen and its operating life would reduce.

A second important requirement is a high oxygen solubility limit to allow many activation-air exposure cycles. When making the realistic assumption that the thickness of the oxide layer formed during air exposure is 2–3 nm, a 1 mm thick film would present an oxygen concentration of 2%–3% after 10 such cycles. Oxygen concentration could be lowered by increasing the film thickness, but to guarantee a reasonable NEG life a solubility limit in the range of 10% or more is desirable. As far as H$_2$ is concerned, to ensure a large pumping capacity at ambient temperature and under UHV conditions the getter should provide high diffusivity, and possibly a hydride phase with low dissociation pressures. Finally, the ideal material should provide large enthalpies of adsorption for all the gases which are usually present inside UHV vacuum systems, i.e. H$_2$, CO, CO$_2$, N$_2$ and O$_2$. In addition to these properties which characterize its ‘‘vacuum behaviour,’’ the selected getter material should also provide other essential features, namely, good adhesion to the substrate, high mechanical resistance, and high melting point (to withstand cathode heating during the coating process). Furthermore, it should be nontoxic, nonpyrophoric, and if possible inexpensive. Finally, in some cases (e.g., for use in particle accelerators) it should also be nonmagnetic and present a low photoelectric and secondary electron yield to avoid electron emission and multipactoring. All these requirements are best fulfilled by the elements of the column IV B of the periodic table, i.e., Ti, Zr or Hf. The most restrictive requirement is the high solubility limit for oxygen, for which only these elements exceed 10%. Therefore, Ti, Zr, Hf, and some of their binary combinations have been taken as an obvious starting point for the present experimental study. However, it should be noted that another family of elements, namely, the rare earths, fulfilled most of the requirements listed above [10].

3. Target preparation

The targets of Ti-Zr-V (Ti$_{0.5}$Zr$_{0.4}$V$_{0.1}$) alloy used for magnetron sputtering in this investigation were prepared from high purity crystal bar zirconium (having oxygen content less than 1000 ppm), high purity titanium and vanadium. To remove any surface oxide layer, pieces of these metals used for
alloy making were etched in a solution of 12 parts HF, 30 parts HNO₃ and 58 parts H₂O. The etched materials were washed in flowing water, rinsed several times with methanol and dried. The alloys were made by non-consumable arc melting using a tungsten electrode in a water-cooled copper hearth, in a vacuum better than 10⁻³ torr. Each button was melted several times in order to ensure composition homogeneity. Each ingot was weighed after melting to monitor any melting losses. The chemical homogeneity was verified by using an electron probe microanalysis (EPMA) on the buttons. The button was sealed in a mild steel tube under vacuum for hot rolling. The cast structure of the alloy buttons was broken by hot rolling. The multiple pass hot rolling was carried out to obtain the sheet of the alloy.

4. Sample preparation
A small ingot of about 20 mm diameter and a maximum thickness of about 4 mm was used for the present experiments. In order to maintain the stoichiometry it was decided to prepare the films by vacuum arc evaporation at the coating facility as shown in Fig. 1 available with Bangalore Plasmatek. Two electrodes of size ~ 18 x 8 mm were prepared. A dc electric arc was struck between the two in a vacuum of about 6x10⁻⁵ mbar. Films were deposited on cleaned stainless steel substrates. A schematic diagram of the depositing system is shown in fig.1.

5. Sample characterization
The XPS studies were conducted in a UHV chamber (base pressure < 2 x 10⁻⁸ mbar) using a VG make, CLAM-2 model analyzer with a non-monochromatic twin Al/Mg X-ray source. The analyzer was operated in the CAE (Constant Analyzer Energy) or high energy resolution mode. Under these conditions, energy resolutions and chemical shifts could be detected to about ± 0.5 eV. The film samples were studied in as-deposited condition after mounting on a sample manipulator containing heating / cooling arrangements. The films were heated for 2 hrs at different temperatures in steps of 20°C to up to 200°C and then in steps of 50°C up to 500°C and XPS was performed after cooling the sample to room temperature after each cycle. XPS quantitative analysis permitted to determine the alloy stoichiometry. The NEG composition was calculated from Zr 3d and V 3p₃/₂ and Ti 3p₃/₂ peak areas using empirically determined sensitive factors after each activation cycle [11]. The Zr content of non-activated film of NEG decreased after each cycle. The series of V 3p₃/₂, Ti 3p₃/₂, Zr 3d spectra are plotted which showed the different chemical states typical for Ti-Zr-V NEG surface as shown in Fig.2, 3 and 4.

In the case of an oxide film on an air exposed NEG surface (as received samples), all titanium and zirconium atoms appeared to be in states characteristic for titanium and zirconium oxides, with binding energy close to TiO₂ (B.E. Ti⁴⁺ 3p₃/₂ = 456.5 – 455.5 eV) and ZrO₂ (B.E. Zr⁴⁺3d₅/₂ = 182.1–
183.1 eV) as can be seen in Fig. 2, 3 [12, 13]. V 2p$_{3/2}$ spectra in Fig. 4 exhibit several elementary peaks which can be attributed to different oxidation states of vanadium: metallic state (512.1 eV) to some oxide state (514.4 eV) as shown in Fig. 4.

**Fig. 2: XPS of Ti 3p$_{3/2}$ in (a) ‘a-deposited’ Ti-Zr-V film and that in the film treated or 2 hrs under at (b) 100°C, (c) 160°C, (d) 180°C, (e) 200°C (f) 250°C (g) 300°C (h) 350°C (i) 400°C (j) 500°C.**

**Fig. 3: XPS of Zr 3d$_{5/2}$ in (a) ‘a-deposited’ Ti-Zr-V film and that in the film treated for 2 hrs under At (b) 100°C (c) 160°C (d) 180°C (e) 200°C (f) 250°C (g) 300°C (h) 350°C (i) 400°C (j) 500°C.**

**6. RESULTS AND DISCUSSION**

All elementary XPS peaks are shifted by 1 eV to lower BE for Zr, Ti and 2.5 eV for V during the heating to 160°C which can be particularly well seen for zirconium, titanium, vanadium and oxygen. This behaviour can probably be explained by the Fermi level shift during oxide reduction, which should affect all BEs in the same manner. The Zr 3d$_{5/2}$ peak appearing close to 183 eV at room temperature can be associated with the Zr–OH bond formation, due to water dissociation which is in agreement with data reported in Ref. 12 where BE of 183.4 eV is related to Zr–OH bonding. The O1s intensity at 529.7 eV can be attributed to emission from different oxygen containing adsorbates which disappear during outgassing at 120°C. On the other hand, the O1s intensity around 530.2 eV corresponds to the metal oxide and it decreases progressively during the getter activation as shown in Fig. 5. It can be seen that the residual oxygen did not disappear completely from the surface even at 500°C. Oxide of vanadium is reduced more rapidly then ZrO$_2$, by formation of vanadium sub-oxides V$_x$O$_y$.

**Fig. 4: XPS of V 3p$_{3/2}$ in (a) ‘a-deposited’ Ti-Zr-V film and that in the film treated for 2 hrs at (b) 100°C, (c) 160°C, (d) 180°C, (e) 200°C, (f) 250°C, (g) 300°C, (h) 350°C, (i) 400°C and (j) 500°C.**

**Fig. 5: XPS of O 1s in (a) ‘a-deposited’ Ti-Zr-V film and that in the film treated for 2 hrs at (b) 100°C, (c) 160°C, (d) 180°C, (e) 200°C, (f) 250°C, (g) 300°C, (h) 350°C, (i) 400°C and (j) 500°C.**
Fig. 6: Binding energy of Ti 3p$_{3/2}$ in Ti-Zr-V film ‘as deposited’ films and after the films were thermally treated for 2 hrs under UHV at different temperatures.

Fig. 7: Binding energy of Zr 3d$_{5/2}$ in Ti-Zr-V film ‘as deposited’ films and after the films were thermally treated for 2 hrs under UHV at different temperatures.

The conversion of oxide films, T–Zr–VO$_x$, into metallic films due to heat treatment under UHV conditions is termed as ‘activation’ as shown in Fig.6, 7 and 8. The activated metal films when cooled to room temperature start getting and therefore could be used as non-evaporable getters to pump residual gases at that pressure in a chamber. The gases present at the pressure of $10^{-11}$ mbar are H$_2$, CH$_4$, CO and noble gases. We have recorded the XPS spectra of Ti, Zr, V and oxygen in Ti-Zr-V film in ‘as deposited’ state and in the film that was thermally treated at different temperatures in steps of 50°C and lower.

Fig. 8: Binding energy of V 3p$_{3/2}$ in Ti-Zr-V film ‘as deposited’ films and after the films were thermally treated for 2 hrs under UHV at different temperatures.

7. Conclusions

Thin films of Ti–Zr–V alloy were deposited using a DC arc evaporation technique. The XPS studies revealed a lower activation temperature of 160°C for 2 hrs of heating for Ti–Zr–V alloy films compared to Ti–Zr films and pure Zr films. The Ti–Zr–V films can be used as NEG to achieve lower pressures in extreme high vacuum applications.
Ternary Ti-Zr-V activation was seen to proceed by the subsequent transition of oxides (TiO₂, ZrO₂ and V₂O₃) to residual zirconium and vanadium suboxides mixed with metallic Ti, Zr and V phases even at 160°C. Vanadium oxide reduction proceeds at lower temperatures than Zr and Ti. During the activation process, zirconium hydrides and carbides are formed above 200°C. On the other hand, reduction of oxides via their reaction with hydrogen diffusing toward the surface seems to be possible. It would explain the formation of hydroxyls at lower temperature and hydrides at higher temperatures when the oxides are almost reduced. The influence of residual sub-oxides on getter activity is not evident.

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