CHARACTERIZATION OF NEG COATING FOR THE PRODUCTION OF EXTREME HIGH VACUUM

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Abstract

Getters are the materials which are used to provide the surfaces whose outgassing is reduced to very low level. Getters are capable of chemisorbing gas molecules on their active surfaces. They are widely used for variety of applications such as in accelerators, vacuum tubes, field-emission display (FED), inert gas purification systems, H2 plasma purification, hydrogen species recycling as in Tokamak Fusion Reactor. In the present investigation, Ti-Zr-V coating of different compositions have been deposited by DC (Direct-Current) diode magnetron sputtering. The influence of the film composition, on the activation temperature have been investigated in order to optimize the deposition parameters for vacuum applications. Coatings of NEG (Non Evaporable Getters) on metallic substrate such as stainless steel or copper are very useful to achieve Extreme High Vacuum. The pressure which suits the term extreme high vacuum is lower than 10^{-11} mbar. This order of pressure is extremely important in high energy particle accelerators as well as Synchrotrons, e.g. LHC, Photon Factories. In LHC the pressure in the interaction region of the two beams is something of the order of 10^{-12} mbar. In this paper preparation of the coatings and their characterization with the surface techniques X-ray Photoelectron Spectroscopy (XPS), Energy dispersive X-ray spectroscopy (EDX) and Scanning Electron microscopy (SEM) have been shown. Characterization techniques shows that these type of coatings can be activated by heating of 160-180 degree C.

Key words: Extreme high Vacuum, NEG

Introduction

It is obvious that surface outgassing is the main culprit to achieve ultrahigh vacuum (UHV) 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 gases, mainly H₂, CO, CO₂ and CH₄. As in modern UHV technology, continuous efforts has been done to reduce surface outgassing. H₂ is the main problem when the pressure is below 10^{-10} torr because H₂ being very small size diffuse in the bulk of the material during the processing of the material itself. This H₂ is a very prominent source of outgassing due to pressure difference when the pressure goes below 10^{-10} torr. 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 [1-2]. 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. In this paper, It has been describe target preparation in alloy forms using pure Ti, Zr, and V metals, preparation of Ti – Zr – V NEG...
thin films by DC magnetron sputtering system and results of characterization using XPS and SEM techniques for film thermally treated at different temperatures to understand the activation mechanism.

Selection of Getter Materials

During the activation of a NEG coated on stainless steel, the present surface oxides 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 bakeout. In both cases, the getter film would otherwise be unduly loaded with oxygen and its operating life reduced.

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.

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.

The other requirement is the high oxygen diffusion coefficient of materials. This requirement is fulfilled by the elements of group VB (V, Nb and Ta). The binary and ternary combination of these in alloy forms when sputtered coated on the inner surfaces of the vacuum subsystems provide the suitable activation temperature.

Sputtering

Sputtering is ideally suitable for NEG coating. It is simple and applicable for wide range of materials and alloys, stoichiometry of which it preserves. It allows uniform and distributed coating of long, narrow vacuum chambers and can produce alloys/compounds by using composite cathodes.

NEG coating on ss304 substrate was prepared by DC magnetron sputtering method. Substrate cleaning is the major issue for better sticking of the film. First substrate of size 300X250 mm² was cleaned by soap solution using ultrasonic bath, this removes the oil contaminant on the surface. After soap solution it was again ultrasonically cleaned with water which removes the soap contaminant. It is dried using UV lamp, so that water could go out from the substrate surfaces. After drying it was again ultrasonically cleaned using acetone solution.

A DC magnetron sputtering configuration has been employed and photograph has shown in Fig.1. The cathode (target) is made by twisting wires of metals Ti, Zr and V with the purity of 99.8%. The required magnetic field is produced by an external solenoid, co-axial to the cylindrical sample. All samples have been produced using the same parameters, namely, a magnetic field of ~ 200G, Acathode voltage of -200V, substrate at ground, base pressure was 2X10⁻⁶ Torr and argon pressure of 1.1 X 10⁻² Torr.

Fig.1: Photograph of the cylindrical shape DC magnetron sputtering system
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 of 150 ºC, 180ºC, 250 ºC and 300 ºC and then 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 3p₅/₂ peak areas using empirically determined sensitive factors after each activation cycle. The series of V 3p₃/₂, Ti 3p₅/₂ Zr 3d spectra are plotted which showed the different chemical states typical for Ti-Zr-V NEG surface as shown in Figs. 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 Ti(B.E. Ti⁴⁺ 3p₃/₂ = 457–454 eV) and ZrO₂ (B.E. Zr⁴⁺ 3d₅/₂ = 183–181 eV) as can be seen in Fig. 2, 3. V 2p₅/₂ spectra in Fig. 2 exhibit several elementary peaks which can be attributed to different oxidation states Vⁿ⁺ from vanadium metallic state (512.1 eV) to some oxide state (514.4 eV) as shown in Fig. 2.

Result

XPS spectra of the Ti-V-Zr film has been taken as-deposited and at different temperatures (rt, 150, 180, 250, 300 ºC) after 2 hrs of heating at each temperature. XPS results as shown in Fig. 2 in the change of the oxidation states of the V at about 150ºC. A shift of 2.0 eV has been resulted in the peak 3d₅/₂ of Vanadium oxide after 150ºC and reach to 3.0 eV at the temperature of 180ºC. The shift in the peak corresponds to lower oxidation state and metallic state. In Fig. 3 the energy value of Zr(3d₅/₂) peak corresponds to ZrO₂ in Ti-Zr alloy in as-deposited film. There is a shift of 1.0 eV in the oxidation state of the Zr(3d5/2) after two hrs of heating at different temperatures.

In Fig. 4 the energy value of Ti(3p₅/₂) peak corresponds to TiO₂ in Ti-Zr alloy as-deposited film. There is a shift of 2.0 eV in the oxidation state of the Ti(2p₅/₂) after two hrs of heating at 180ºC.

SEM micrograph of both heated and as-deposited samples in Fig. 6(a) and 6(b) shows no microstructure, the deposited film can be nanocrystalline. After heating the change in the surface can be seen in Fig. 6(a). This type of structure are more prone to diffuse surface oxygen in
the bulk. The change in the surface oxygen of the film has been shown in Fig. 7 after heating at different temperature. Intensity versus temperature plot from XPS data at different temperature, clearly shows the decrease in surface oxygen.

Conclusion

Coatings of NEG materials in ternary from (Ti-Zr-V) alloy were deposited using a DC magnetron sputtering technique. The XPS studies shows the lowest achievable activation temperature is lies in the range of 150°C to 180°C for 2 hrs of heating for Ti-Zr-V 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 V₂O₅) to residual zirconium and vanadium suboxides mixed with metallic Ti, Zr and V phases even at 150°C. This oxide reduction leads to formation of active surface for H₂ and CO to form hydrides and results the lowering of the pressure inside the chambers.

References