Thin films of Ti–Nb–Zr as non-evaporable getter films

R.K. Sharma, Jagannath, S. Bhattacharya, S.C. Gadkari, R. Mukund and S. K. Gupta

Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Email: rajendra@barc.gov.in, Tel: +91 22 25592246

Abstract. Thin films of Non-evaporable getter (NEG) Ti–Nb–Zr, have been deposited using a DC magnetron sputtering technique. The NEG films were produced from a Ti–Nb–Zr target in the form twisted wires of pure individual metals combined to give the appropriate stoichiometry. The performance and morphology dependence on deposition pressure, sputtering conditions and substrate surface roughness are investigated. Energy dispersive X-ray and X-ray photoelectron spectroscopic techniques are utilized to characterize and study the activation behaviour of the NEG thin films. After characterizing with surface techniques the activation temperature of this alloy is found to be in the range 250 – 300°C for 2 h heating with well defined composition. It is seen that film topography and density depend largely on the substrate surface roughness, while the activation temperature depends almost exclusively on the final stoichiometry of the thin film.

1. Introduction
Production of extreme high vacuum (XHV) (pressure ≤ 10^{-10} Pa) is a technologically challenging task. Many of the modern particle accelerators as well as conventional analytical instruments have been pushing the limits of producing XHV that gives several advantages in terms of clean vacuum conditions[1-4]. Surfaces coated with Non evaparable getter(NEG) films have been known to selectively adsorb hydrogen and are being utilized either in the form of stand-alone pumps or more recently as thin film coated vacuum chambers that effectively reduce the partial pressure of hydrogen at very low pressures[5,6].

It is well known that the lifetime of a charged particle beam in storage rings depends mainly on the presence of residual gas molecules and beam instabilities. The conventional method of reducing residual gas molecules is through vacuum pumps located discretely at chosen positions in order to reduce interference with the charged particle beams. The disadvantage of this method is the lack of uniformity of vacuum conditions between two pumps especially in the case of long pipe sections. In order to overcome this disadvantage, it has been proposed to coat the inner walls of the vacuum chambers or pipes with thin films of suitable NEG materials. Active gases such as CO, CO₂, H₂O, N₂, and O₂ are chemisorbed on the NEG surface while H₂ diffuses into the getter bulk, thereby acting like a long continuous pump. Noble gases and CH₄ are not pumped by NEG materials. After in situ activation through the conventional baking procedure, these films provide large pumping speeds and also much lower dynamic and static degassing compared to traditional structural materials.

Activation of the NEG proceeds by heating to a temperature where the native oxide layer on the surface is dissolved into the bulk [7]. The suitability of the NEG for coating on the inner walls of vacuum chambers is given by its lower activation temperature and adhesion of the NEG films on to the substrate. Thus by effectively reducing surface outgassing and creating additional pumping,
production of very low pressures is achieved. Further, the desorption caused by the synchrotron radiation is very low in case of NEG coated surfaces compared to uncoated stainless steel surfaces. However, the sorption capacity for gases, except H₂, is limited to between 1 and 10 mL. This means that the materials suitable for use as an NEG coating should have large oxygen diffusivity, high oxygen solubility at bakeout temperature. The material should also have high sorption capacity and low dissociation probability for H₂. Alloys of Ti, Zr, and Nb fulfil all these requirements. Ti and Zr have an oxygen solubility of greater than 10%, but they have low oxygen diffusion coefficients. Niobium is the opposite case. Hence alloying Nb with any of other elements either in binary or ternary form is most efficient.

In this paper we present the characterization studies of a alloy getter material Ti-Nb-Zr deposited on stainless steel substrate to get a better understanding of the pumping properties of these coatings. The film stoichiometry, activation temperature of the NEG is also reported. It is seen that film morphology depends critically on deposition parameters such as pressure, sputtering conditions, and the substrate surface roughness.

2. Experimental details

We have used DC sputter deposition technique to deposit thin films of NEG material, since sputtering is simple and applicable to a wide range of the materials and alloys as well preserving the stoichiometry. Sputtering also allows uniform and distributed coating of long narrow vacuum chambers and also good adhesion. By employing composite cathodes it is possible to produce thin films of alloys/compounds of different materials. This feature is very attractive since elemental materials are easily available, and also coatings of pyrophoric materials could safely be produced from suitable targets. Once deposited as a thin film the danger of pyrophoricity is circumvented by the thermal capacity of the substrate, which limits the getter heating which results from exothermic gas absorption. Schematic of the DC magnetron sputtering deposition system has been shown in Fig.1

Here, we describe our indigenously fabricated cylindrical type DC magnetron sputtering system specially developed for depositing thin films of NEG materials on long thin SS sheets. Fig.1 shows a schematic of our experimental setup. In order to deposit NEG materials on long thin SS sheets, a substrate holder in a cylindrical form of 100mm diameter and length 300mm was utilized. A multi-turn, high current cooled solenoid was utilized to produce the magnetic field required for confining the plasma discharge. By varying the current through the solenoid, it was possible to produce uniform magnetic fields in the range of 100 – 300 gauss. The NEG target was prepared from a set of inter-twisted wires of diameter 1 mm from high purity (purity > 99.9%) materials of Ti, Zr and Nb in ternary form. Prior to initiating deposition, surface cleaning of the target and the substrate was performed by sonication with soap solution, followed by rinsing in clean distilled water.

The entire setup along with the target and the substrate was initially pumped down using a 500 l/s turbomolecular pump to a base pressure of 2 × 10⁻⁴ Pa. High purity, Lab grade argon was introduced through a leak valve to initiate the discharge. The pressure of sputtering gas Ar was about 1.1Pa. Discharge was initiated in the argon environment using a current stabilized high voltage power supply.
The sputtering parameters were optimized to 200V, 30mA and 0.02Tesla. The distance between the target and the substrate (sheet of 304L stainless steel of 100mm dia and length 300 mm) was 50 mm over the entire length of the target. In order to avoid the sagging of the target due to heating, the target was tensioned with the help of a spring on one side. Under these conditions, a coating rate of about 1 Å/sec was achieved. The film thickness as monitored by quartz crystal thickness monitor was 1 micron(approx.) for 3 hrs of deposition.

3. Characterization

An Oxford Instruments made Energy dispersive X-ray(EDX) instrument was utilized to identify the surface composition of the thin film is shown in table.1 indicating an elemental composition of (Ti 20Zr25Nb55 at.%).

X-ray Photo electron spectroscopy (XPS) measurements were conducted for characterizing the activation properties of the NEG film. Characterization of Ti-Zr-Nb film was performed by (SPECS make XR 50 twin X-ray source). During NEG activation under ultra high vacuum conditions, the surface oxygen content is progressively reduced and surface starts pumping. Activation is completed when the oxygen surface content reaches a minimum and the pumping speed reaches its maximum value.

An Mg \( K_{\alpha} \) X-ray source with 1253.6 eV was used with a detection resolution of concentration of 1 at.%. The detectable signal depth of the sample was better than 5 nm. The base pressure of the experimental chamber was 1.5 \( \times \) 10\(^{-8}\) mbar during the measurement. XP spectra were obtained with a VG Scienta made spectrometer with single channeltron detector having a resolution of < 1 eV. A Thermo Vacuum Generator make sample manipulator (model TX 4570) with heating (upto 1000°C) and cooling down to liquid nitrogen temperature (77K) facilities was employed for controlled sequential heating of the samples. The samples could be rigidly clamped on to the sample holder for good thermal contact with the help of suitable clamps.

The temperature of the sample holder was measured by two K-type thermocouples. In order to study the activation temperature of the NEG films, controlled heating of the sample holder was done through suitable resistive heating element under ultrahigh vacuum conditions. The following procedure was adopted to exactly understand the activation mechanism of the NEG thin film.

4. Results

The high resolution photoelectron spectra allow the metal oxide reduction as a result of heating to be followed. Fig. 2 – 5 show the XP spectra for the Ti-Zr-Nb NEG recorded after heating the sample to different temperatures (25, 100, 120, 140, 180, 200 250 and 300 ºC). The spectrum at 25ºC is the ‘as-deposited’ condition.

Niobium is also the metal which is very easily reduced. The shift in Niobium peak starts at 140 deg C heating, indication the onset of oxide reduction already at this temp. Fig. 2 shows the decomposition of C(1s) to graphitic (atomic) carbon at 285 eV, CO bond at 287 eV, and carbide C-metal bond at 282 eV.
The change of the oxidation state of Ti-Zr-Nb can be seen in the spectra which indicates a transformation from a higher oxidation to lower oxidation state and then to the metallic state. This is clearly seen in Fig. 3 for Niobium. The $3d_{5/2}$ peak of Nb shows a clear shift of 2.5 eV at a temperature of 250°C. The shift in the peak corresponds to lower oxidation state ($\text{NbO}_2$). This peak further shifts to a lower value at a temperature of 300°C.

Fig. 4 shows the evolution of Zr($3d_{5/2}$) peak at different temperatures. There is significant shift in the oxidation state of the Zr($3d_{5/2}$) after 2 h of heating at different temperatures indicating that
the peak corresponds to ZrO\textsubscript{2} in Ti-Zr alloy\cite{6} n the as-deposited film which broadens with temperature. Similar behaviour was found for titanium indicating a Ti – Zr matrix. The oxygen peak in Fig.5 is composed of two elemental intensities at 531 eV and 530 eV. These peaks correspond to different metallic oxides of Ti, Zr and Nb. In Fig.6, the plot between the intensity of the oxygen peak versus temperature using XPS technique shows the oxygen (O1s) evolution with temperature. It can be concluded that in activation of the film surface oxygen diffuses inside the bulk and leave the surface active. From the above observations, it can be concluded that the activation temperature of the NEG coating(Ti-Nb-Zr) will be is in the range of 250 - 300°C.

5. Conclusion
Coatings of NEG materials in the form of ternary alloy of Ti-Zr-Nb were deposited on stainless steel substrate by using a DC magnetron sputtering technique. The XPS studies shows the lowest achievable activation temperature is in the range of 250°C to 300°C for 2 h of heating for Ti-Zr-Nb films. The Ti-Zr-Nb films can be used as NEG to achieve lower pressures in extreme high vacuum applications. Ternary elements Ti-Zr-Nb in the form of alloy was seen to proceed activation by the subsequent transition of oxides (TiO\textsubscript{2}, ZrO\textsubscript{2} and Nb\textsubscript{2}O\textsubscript{3}) to residual zirconium and niobium sub-oxides mixed with metallic Ti, Zr and Nb phases even at 250°C. This oxide reduction leads to formation of active surface for H\textsubscript{2} and CO to form hydrides and results into the lowering of the pressure inside sealed vacuum chambers. The EDX spectrum of the film provides the surface stoichiometry of (Ti\textsubscript{20}Zr\textsubscript{25}Nb\textsubscript{55} at.\%).

All elementary XPS peaks are shifted by about 2 eV to lower BE for Zr(3d\textsubscript{5/2}), 2eV for Ti(2p\textsubscript{3/2}) after heating the sample to 250°C while niobium (Nb 3d\textsubscript{5/2}) B.E. peak is shifted by 3 eV after 250°C.

Acknowledgements
The authors are thankful BARC for giving the support.

Reference
[1] C Benvenuti, P Chiggiato, F. Cicoira, and V Ruzinov, Vacuum 50, 57(1998).
[2] C Benvenuti and F Francia, J. Vac. Sci. Technol. A 6, 2528 (1988).
[3] C Benvenuti and F Francia, J. Vac. Sci. Technol. A 8, 3864 (1990).
[4] C Benvenuti, P Chiggiato, F Cicoira, Y Aminot, and V Ruzinov, Vacuum 73, 139 (2004).
[5] M Sjöström, E Wallén, M Eriksson, and L-J Lindgren, Nucl. Instrum. Methods Phys. Res. A 601, 229 (2009).
[6] J D Herbert, O B Malyshev, K J Middleman, and R J Reid, Vacuum 73, 219 (2004)
[7] Z A Munir, Journal of material Science 14(1979) 2733-2740
[8] C Benvenuti, P Chiggiato, A Mongelluzzo, A Prodromides, V Ruzinov, C Scheuerlein, M Taborelli, and F Levy, J. Vac. Sci. Technol. A 19, 2925(2001).