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Sims study of Ti–Zr–V NEG thermal activation process

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Abstract

In this work, properties of non-evaporable getter (NEG) films prepared on stainless steel substrates by magnetron sputtering were investigated. Changes of the sample surface during thermal activation were studied by means of secondary ion mass spectroscopy (SIMS). Static SIMS observation of a superficial layer as well as dynamic profiling of the surface region were performed.

Two samples of the same Ti:Zr:V stoichiometry were investigated following two different procedures of thermal activation. Step-by-step heating up to 320 °C (as model activation) and direct long time heating to 240 °C (continuous thermal activation) were applied. The SSIMS measurements are highly surface sensitive and reflect changes of the superficial oxide layer covering air-exposed surfaces during activation. To compare the final states of activation, depth profiles of surface layers have been used as well. Molecular ion intensity ratios MX^+/M^+ (X = O, H; M = Ti, Zr, V) have been considered to be directly coverage-sensitive and were monitored during the processes. The results were checked by comparison to corresponding XPS experiments.

Keywords: Static SIMS; Dynamic SIMS; Thermal activation; Titanium; Zirconium; Vanadium; Alloy; Coating; NEG; Getter

1. Introduction

Non-evaporable getters (NEG) steadily increase their importance in the gettering materials group. Many different kinds of getter materials have been developed in the past. In the gettering process not only pure metals (Ti, Ba, Ta, etc.) are used, but binary and ternary alloys are often prepared to achieve special gettering properties. The multi-component alloys exhibit different characteristics depending on the type and stoichiometry of the alloying elements.

NEG are used as active pumping systems to achieve extra-high vacuum (XHV) conditions of 10^{-11} mbar and lower. They can be used for efficient pumping of low-aperture and sealed-off vacuum devices [1–3] or to construct getter pumps as a complement to conventional pumping equipment [4–6]. One of the most important applications

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of NEGs is the reduction of ultimate pressures in collider facilities [1,7–10]. Pumping characteristics and activation temperature are the most important parameters which determine fields for the practical use of NEGs.

Many NEGs composed of various elements have been tested in order to obtain a low activation temperature, to enlarge the fields for getter applications. Some Zr–V binaries and Ti–Zr–V ternaries have been found to exhibit an activation temperature around and below 200 °C [11]. The thin layer NEG coating of nearly all UHV chamber walls, activated during bakeout of the system, is one of the best applications. Recently, several studies have been devoted to the characterisation of Ti–Zr–V getters by means of surface sensitive techniques, which showed good applicability of Auger electron spectroscopy (AES) [11,12], X-ray photoelectron spectroscopy (XPS) [13,14] and static secondary ion mass spectroscopy (SSIMS) in this field [15,23–26]. XPS investigations showed that oxide reduction proceeds through formation of sub-oxides with simultaneous formation of carbides [26,27] in the near surface region. The SSIMS technique is a powerful tool for NEG surface examination due to its high surface sensitivity. It makes SSIMS particularly suitable for investigations of gas interactions with the getter surface. One important feature of SSIMS is to monitor hydrogen and hydrides which cannot be measured by XPS. Dynamic SIMS (DSIMS) studies can show the depth profiles of chosen elements. Oxide samples are advantageous for this method because of the high yield of secondary ions.

In this paper, we compare the step-by-step activation process (used mainly for research purposes) and long time heating at a given temperature (close to real use activation conditions during bakeout of the UHV system). The progress of the activation as well as conditions of the activated layer were compared.

2. Experiment

Ti–Zr–V getter films have been prepared on stainless steel substrates by coaxial DC magnetron sputtering. The cathode consists of three twisted wires of the pure metals Ti, Zr and V. Sputtering condition: Ar pressure of 0.6 Pa, Ar^+ ion current density of $3\,mA/cm^2$, high voltage of 500 V, deposition time of 10 min. The present composition of the sample as measured by XPS was 25% Ti, 50% Zr and 25% V. This NEG sample stoichiometry was chosen because it belongs to the best group of Ti–Zr–V based NEGs (low activation temperature, high capacity) [11,22].

The SSIMS experiments were performed in an UHV chamber equipped with a Perkin-Elmer spectrometer Phi 06–600 and a differentially pumped Ar-ion gun PU-IQ 12/38 from Specs. The residual gas composition was monitored by a Balzers-Prisma 200 QMS. The base pressure was typically around 8×10^{-11} mbar and the working pressure was 5×10^{-9} mbar during SIMS measurements. The main components of the residual gas were H_2, Ar and CO. The sample was mounted on a Mo sample holder and heated by a low-degassing boron–nitride–graphite heating element. The temperature was controlled by a PC-controlled heating system.

Initially, SSIMS scan and dynamic SIMS depth profile were taken. The air-exposed samples were degassed at 120 °C for 4 h and SSIMS spectra were taken again. After this step, two different types of activation were used. The step-by-step thermal activation process was performed in five consecutive heating steps at 160, 200, 240, 280 and 320 °C. In each cycle, the sample was kept at the indicated temperature for 2 h (SSIMS spectra were recorded at the given temperature at the end of each heating step). The continuous thermal activation process starts by fast heating to 240 °C and then keeping this temperature for 20 h. The activation process was investigated by recording SSIMS spectra continuously for 2 h. A final SSIMS scan was taken at the end of the activation period (20 h).

SSIMS was operated at very low current density and energy of the primary Ar^+-ion beam ($1000\,eV, < 5\,nA\,cm^{-2}$) in order to preserve chemical integrity of the analysed surface during measurements. The size of the analysed area during SSIMS experiments was $16\,mm^2$. DSIMS was operated at a higher primary ion current density and energy ($3000\,eV,\ 500\,nA\,cm^{-2}$). The