

# THE SECONDARY ELECTRON YIELD FROM TRANSITION METALS

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## Abstract

Non-evaporable getter (NEG) thin films, which are currently being used in the ultra-high vacuum system of the Large Hadron Collider (LHC), normally consist of Ti, Zr and V, deposited by physical vapour deposition (PVD). In this study, the secondary electron yield (SEY) of bulk Ti, Zr, V and Hf have been investigated as a function of electron conditioning. The maximum SEYs of as-received Ti, Zr, V and Hf, are respectively 1.96, 2.34, 1.72 and 2.32, these reduce to 1.14, 1.13, 1.44 and 1.18 after electron conditioning. Surface chemical composition was studied by X-ray photoelectron spectroscopy (XPS) which revealed that surface conditioning by electron bombardment promotes the growth of a thin carbon layer on the surface and consequently reduces the SEY of the surface as a function of electron dose. Heating a vanadium sample to 250 °C resulted in diffusion of oxygen into the bulk and induced formation of metal carbide at the surface. However, the SEY stays the same even after heat-induced surface chemistry modification. Prolonged electron conditioning increases the surface oxygen but the surface is still predominantly covered with a thin graphitic layer and hence the SEY stays approximately constant.

## INTRODUCTION

Electron cloud is one of the limitations for operating particle accelerators with positively charged beams of high-intensity and short bunch spacing. Electrons originate from ionised residual gas molecules, by photoemission and by secondary electron emission from the vacuum chamber walls. They may move resonantly with beam bunches and can collide with both the charged particle beam and the walls in the vacuum chamber.

If the SEY of the vacuum chamber is larger than unity then electron multipacting may occur [1,2]. The SEY is one of the key parameters controlling electron cloud build-up in the particle accelerators and NEG coatings (after *in-situ* baking) not only provide valuable pumping and reduction of outgassing but they also have a low SEY [3]. NEG films are usually composed of a mixture of Ti, Zr, V and Hf. The literature values for the SEY of atomically clean Ti and Zr are 0.9 and 1.1, respectively [3]. However, oxide contamination layers are formed if the surfaces are exposed to air and as a result the SEY of

vacuum component metal surfaces are usually higher than those of sputter cleaned metal surfaces [3]. The SEY of air-exposed metals can be decreased by different surface treatments such as electron conditioning, *in-situ* vacuum bakeouts and ion bombardment.

The aim of this work was to study the SEYs of the transition metals Ti, Zr, V and Hf as a function of electron beam exposure (conditioning) and thermal treatment alongside with XPS analysis of the surface chemical composition.

## EXPERIMENTAL

The SEY measurements were carried out in a new, dedicated setup a schematic of which is shown in Figure 1.

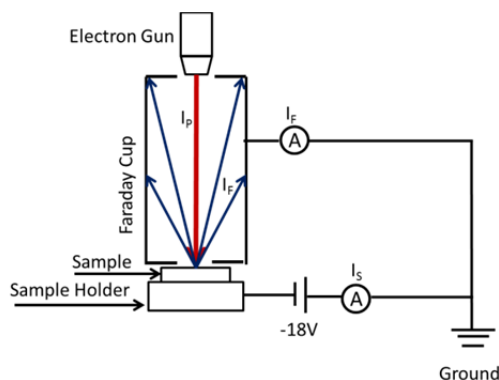


Figure 1: Schematic layout of the SEY apparatus.

The total SEY,  $\delta$ , is defined as

$$\delta = \frac{I_F}{I_P} = \frac{I_F}{I_F + I_S} \quad (1)$$

where  $I_S$  is the secondary electron current (including both elastic and inelastic processes) measured at the sample,  $I_F$  is the current on the Faraday cup and  $I_P$  is the primary beam current.

All samples (dimensions  $\sim 12 \times 12$  mm<sup>2</sup>) were glued to the sample holder by conductive silver epoxy (M.E. Taylor Engineering Inc., USA). The Ti, Zr, V and Hf purities were 99.6%, 99.2%, 99.8%, and 97%, respectively. A VG flood gun was used for electron conditioning (electron energy 485 eV) prior to the SEY measurements. The accuracy of the electron dose from this was to within 10%.

The SEY as a function of primary electron energy was measured over the range 80 to 1000 eV and at normal incidence. Measurements were performed using a

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Kimball electron gun (ELG-2/EGPS-2). The pressure in the test chamber was  $2 \times 10^{-10}$  mbar without electron bombardment and  $2.5 \times 10^{-9}$  mbar during electron bombardment. The net current at the sample biased at  $-18$  V and the Faraday cup at ground potential were measured with two current amplifiers (Keithley 6517A and Keithley 6485, with an accuracy  $\pm 0.01\%$ ). As the SEY is very sensitive to the electron dose, the total electron dose during the SEY measurements, as a function of primary energy, was not allowed to exceed  $10^{-6}$  C $\cdot$ mm $^{-2}$ . The accuracy of the SEY measurements was estimated to be within 1% for primary electron energies between 80 and 800 eV and about 6% for primary electron energies above 800 eV.

The experimental procedure involved initial measurement of the SEY of the as-received sample followed by repeated conditioning with the diffuse-beamed electron flood gun to the doses indicated. After each conditioning, the energy dependence of the SEYs was re-measured. The as-received V sample was in addition first conditioned with an electron dose of  $1.2 \times 10^{-3}$  C $\cdot$ mm $^{-2}$  then heat treated (thermal activation) to  $250$  °C for 2 hours before further, prolonged, conditioning with an electron dose of  $7.0 \times 10^{-3}$  C $\cdot$ mm $^{-2}$ . The photoemission spectrum was recorded at each stage.

## RESULTS AND DISCUSSION

As observed previously we found that the SEY decreases when the surface is subjected to electron beam bombardment [4]. In Figures 2-5, the SEYs of as-received Ti, Zr, V and Hf are plotted as a function of primary electron energy showing variation with electron dose. The materials all exhibit the same overall SEY behaviour *viz.* rising from values obtained with low primary electron energy to a maximum at a few hundred electron volts followed by a steady decline. The maximum SEYs ( $\delta_{max}$ ) of as-received Ti, Zr, V and Hf were 1.96, 2.34, 1.72 and 2.32, respectively. In all cases the  $\delta_{max}$  moves to lower primary electron energy with electron dose; this effect is particularly clear for Zr and noticeably less prominent for V.

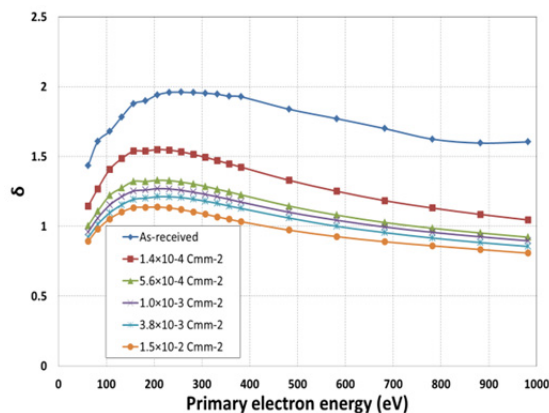


Figure 2: SEY reduction of Ti as a function of primary electron energy showing variation with electron dose.

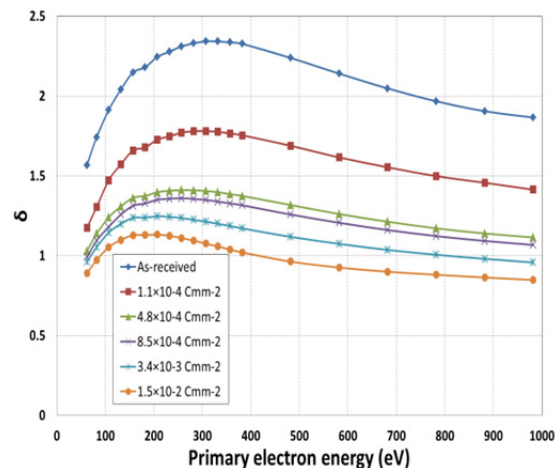


Figure 3: SEY reduction of Zr as a function of primary electron energy showing variation with electron dose.

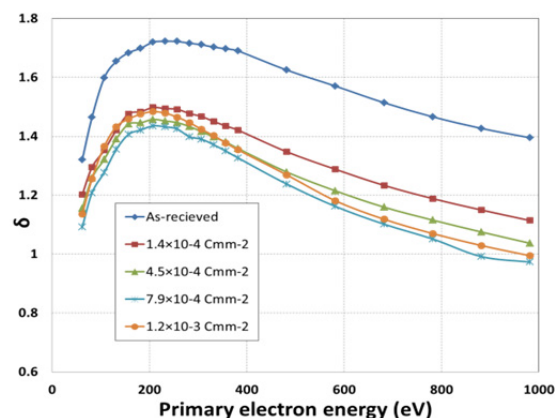


Figure 4: SEY reduction of V as a function of primary electron energy showing variation with electron dose.

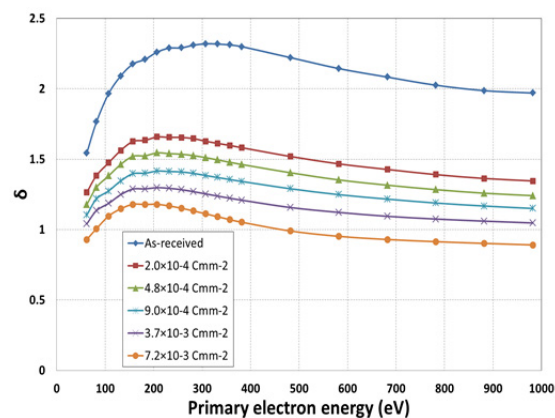


Figure 5: SEY reduction of Hf as a function of primary electron energy showing variation with electron dose.

The initial drop in the SEY with electron dose is larger than subsequent decreases. The V sample exhibits a large change in SEY with initial primary electron dose and then very little difference. After a dose of  $1.5 \times 10^{-2}$  C $\cdot$ mm $^{-2}$ ,  $\delta_{max}$  of Ti drops to 1.14 and that of Zr drops to 1.13.  $\delta_{max}$  for V and Hf drop to 1.48 and 1.18 after doses of  $1.2 \times 10^{-3}$  and  $7.2 \times 10^{-3}$  C $\cdot$ mm $^{-2}$ , respectively.

The XPS surface characterisation studies were started with an investigation on the V sample, see Figure 6. The as-received sample (spectrum (1)) was first conditioned with an electron dose of  $1.2 \times 10^{-3} \text{ C}\cdot\text{mm}^{-2}$  (spectrum (2)) then heat treated to  $250^\circ\text{C}$  (spectrum (3)) before further, prolonged, conditioning with an electron dose of  $7.0 \times 10^{-3} \text{ C}\cdot\text{mm}^{-2}$  (spectrum (4)). Considering first the spectrum of the as-received V sample there are, as expected, strong C and O peaks. The C1s peak is at binding energy of 286.3 eV, which is attributed to CO. The  $\text{V}2\text{p}_{3/2}$  and  $\text{V}2\text{p}_{1/2}$  peaks are very weak and shifted to 517.0 and 523.9 eV, respectively, indicating the presence of  $\text{V}_2\text{O}_5$ . An electron bombardment dose of  $1.2 \times 10^{-3} \text{ C}\cdot\text{mm}^{-2}$  shifts the C1s peak to 285.1 eV which is associated with graphitic carbon [2,5]. The presence of the oxygen peak and the positions of the vanadium peaks indicate that  $\text{V}_2\text{O}_5$  is still present at the surface. Further, the XPS results reveal a reduction in the intensity of the oxygen and vanadium peaks compared with those of the as-received V sample. This is believed to be a consequence of the growth of a thin graphitic film on the surface rather than reduction of oxygen within the original surface layer. We conclude therefore that on electron conditioning the SEY is reduced because of a thin carbon layer on the surface.

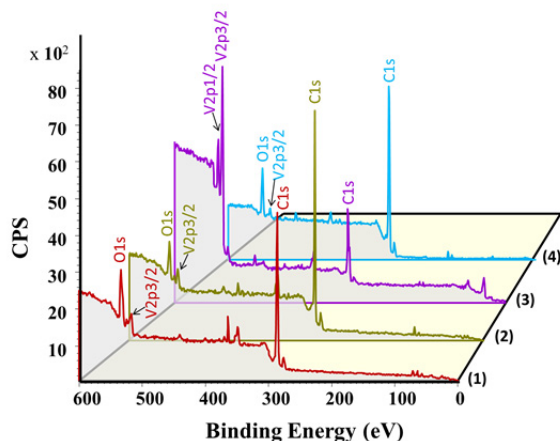


Figure 6: The XPS spectra of the V sample (1) as-received, (2) after an electron dose of  $1.2 \times 10^{-3} \text{ C}\cdot\text{mm}^{-2}$ , (3) after thermal treatment to  $250^\circ\text{C}$  and (4) after prolonged electron conditioning (dose  $7.0 \times 10^{-3} \text{ C}\cdot\text{mm}^{-2}$ ).

After heat treatment, Spectrum 3, the oxygen peak has dropped dramatically in intensity and  $\text{V}2\text{p}_{3/2}$  and  $\text{V}2\text{p}_{1/2}$  peaks have moved to the metallic V binding energies of 512.8 and 520.3 eV.  $\text{V}3\text{p}$  and  $\text{V}3\text{s}$  peaks are also obvious in the spectrum. In addition to the graphitic carbon peak at 284.4 eV, there is a low-energy shoulder at 282.0 eV which is assigned to vanadium carbide. Additional peaks have been assigned to Ti and Ca bulk impurities. Overall, these observations were attributed to oxygen diffusing into the metal.

After prolonged conditioning (Spectrum 4) the V peak positions and the V-to-O peak ratio in the X-ray photoemission spectrum indicates that sample surface has

once again significant amounts of  $\text{V}_2\text{O}_5$ . However, a graphitic carbon peak at 284.4 eV points to the fact that this still exists in the surface layer.

Figure 7 shows the SEYs of the vanadium sample after thermal activation and final prolonged conditioning.

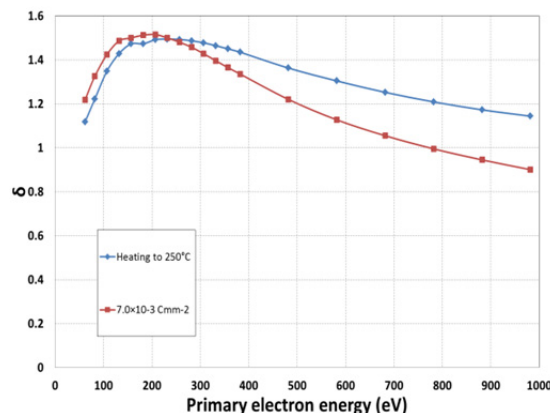


Figure 7: SEY of V after heat treatment and final prolonged conditioning.

The maximum SEY of the V sample after thermal activation is 1.49, that after prolonged electron conditioning is very similar at 1.51. XPS results after prolonged electron conditioning show that both the oxygen intensity increases (which should lead to a rise in SEY) and that graphitic-carbon is present (which should lead to a reduction in SEY). Taken together these two results indicate that the SEY is influenced by the top of graphitic carbon layer rather than the oxygen density on the surface.

## CONCLUSIONS

The maximum SEYs of as-received Ti, Zr, V and Hf samples, are 1.96, 2.34, 1.72 and 2.32 respectively. These results are higher than those for atomically clean metals because oxide contamination layers are formed on air exposure. Electron conditioning reduces the SEYs by producing a graphitic carbon layer at the surface rather than by removing oxygen. Thermal activation causes the oxygen to diffuse from the surface into the metal bulk and promotes the transformation of fraction of the graphitic-carbon into metal carbide. The SEYs after heat treatment and then prolonged electron conditioning are almost the same due to a carbon layer on the surface.

## REFERENCES

- [1] F. Le Pimpec et al., Nucl. Inst. Meth. A 551, 187 (2005).
- [2] R. Cimino et al., Phys. Rev. Lett. 109 064801 (2012).
- [3] B. Henrist et al., Appl. Surf. Sci. 172, 95 (2001).
- [4] V. Baglin et al., Proc. EPAC2000, p. 217 (2000); <http://jacow.org>
- [5] D.R. Grosso et al., Phys. Rev. ST-AB 16, 051003 (2013).