

# EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

## CERN – EST

CERN EST/2002-003 (SM)

### **The secondary electron yield of air exposed metal surfaces at the example of niobium**

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#### *Abstract*

The secondary electron yield (SEY) variation of atomically clean metal surfaces due to air exposures and during subsequent heat treatments is described with the example of a sputter-deposited Nb thin film. Corresponding variations of the surface chemical composition have been monitored using AES and SSIMS. On the basis of these results and of previously obtained SEY results on metals and metal oxides the origin of the SEY variations is discussed.

The SEY increase, which is generally observed during long lasting air exposures of clean metals, is mainly caused by the adsorption of an airborne carbonaceous contamination layer. The estimated value of about 3 for the maximum SEY of this layer is higher than that of all pure metals.

Only in some cases the air-formed oxide can contribute to the air exposure induced SEY increase while many oxides have a lower SEY than their parent metals. From the experimental data it can also be excluded that the SEY increase during air exposures is mainly due to an increased secondary electron escape probability.

*Paper submitted to Applied Physics A*

*Geneva, Switzerland*

June 2002

## 1. INTRODUCTION

The secondary electron yield (SEY) of the internal surfaces of ultra high vacuum systems is of great importance for devices the operation of which can be perturbed by the occurrence of a resonant electron multiplication (multipacting) [1]. Examples for such devices are superconducting RF cavities for particle acceleration [2], and the beam vacuum system of CERN's next accelerator, the Large Hadron Collider (LHC) [3].

Reliable SEY data for most atomically clean metals have been published already several decades ago [4]. However, despite the fact that for many applications the SEY of air exposed surfaces is more relevant than the SEY of atomically clean surfaces, SEY data of air exposed surfaces are rare and the reasons for the SEY variation during air exposures of atomically clean metals are still discussed controversially. There are mainly two reasons for this.

Firstly, it is difficult to define precisely an air exposed surface because of the many parameters influencing the surface properties (e.g. initial sample state, air exposure time, humidity, concentration of contaminants in the ambient air, etc.). For initially clean copper, as an example, the maximum SEY value after air exposure can vary between 1.2 and above 2 for an air exposure lasting a few minutes and a few days, respectively [5].

The second reason why SEY data of air exposed surfaces is often questionable is the fact that the SEY of such surfaces is much more sensitive to electron irradiation than the SEY of atomically clean surfaces [6]. Electron doses as low as  $10^{-6}$  C mm<sup>-2</sup> remove efficiently a part of the surface species and, as a result, reduce the SEY [7]. Therefore, measurements on air exposed metal surfaces provide in some cases the SEY of an electron beam damaged surface, which has a much lower SEY than the as-received surface.

Several SEY and surface analysis measurements of differently treated air exposed Nb surfaces have been reported [8,9]. However, the effect of an air exposure on the SEY can be evaluated at best on a sample that is atomically clean before the air exposure. In the present study this has been achieved by preparing a clean Nb coating under vacuum by sputter-deposition.

The influence of thermal treatments on the SEY has been measured and the results are compared with SEY results, which have been obtained previously on chemically polished Nb with the same experimental set-up [8]. In parallel variations of the surface composition are monitored by Auger electron spectroscopy (AES) and by Static Secondary Ion Mass Spectroscopy (SSIMS).

Based on the present experimental results obtained for Nb and on previous data for other metals and metal oxides, the reasons for the SEY increase during air exposure of atomically clean metals and the effect of the heat-treatments on the SEY are discussed.

## 2. EXPERIMENTAL SET-UP AND PROCEDURES

### 2.1 Sample preparation

The Nb sample studied is in the form of a thin film, of the type used as a superconducting coating in radiofrequency cavities for particle acceleration. The 1.5  $\mu\text{m}$  thick Nb thin film is deposited onto a chemically polished OFE copper substrate by magnetron sputtering inside a cavity. For more information about the Nb coatings see reference 2. After sputter deposition the Nb thin films are vented to atmospheric pressure with a dry O<sub>2</sub>/N<sub>2</sub> mixture and exposure to ordinary laboratory air before introducing the samples into the

vacuum chamber of the various analytical systems lasted then about 2 hours. In Figure 1 the surface topography of the Nb thin film as observed with a scanning electron microscope is shown.

## 2.2 SEY measurements

SEY measurements are carried out with a dedicated instrument, which is described in reference 5. The used experimental set-up has been designed to allow SEY measurements using very low primary electron (PE) doses. For the SEY measurements presented here the total PE dose which is accumulated during the acquisition of one SEY versus PE energy spectrum (at 60 different PE energies) is about  $10^{-8}$  C mm<sup>-2</sup>.

## 2.3 Auger electron spectroscopy

The variation of elemental surface composition as a function of thermal treatments is monitored by AES, as described in reference 10.

The electron dose which is typically accumulated during the acquisition of a single Auger survey spectrum is in the order of  $10^{-3}$  C mm<sup>-2</sup>. Contrary to the SEY and SSIMS measurements presented, the AES measurements are obscured by beam damage. By electron dose dependent AES measurements on an air exposed Nb thin film it has been shown [7] that the main effect of the electron irradiation is the electron stimulated desorption of hydrocarbon species, which is indicated by a strong Nb-MNV peak intensity increase. The C-KLL peak intensity on an air exposed Nb thin film decreases by about 30 % during  $10^{-4}$  C mm<sup>-2</sup> electron exposure, directly showing the removal of carbon. These electron induced surface modifications cause a drastic reduction of the SEY.

During sample heating the total pressure in the vacuum chambers of the SEY and AES experiments increases up to about  $5 \times 10^{-6}$  Pa, with H<sub>2</sub> being the main gas followed by H<sub>2</sub>O and CH<sub>4</sub> (partial pressures p<sub>H<sub>2</sub>O</sub> and p<sub>CH<sub>4</sub></sub>  $\approx 5 \times 10^{-7}$  Pa). The CO and CO<sub>2</sub> partial pressures are both in the order of  $10^{-7}$  Pa. The sample heater assemblies and the heating procedures are described in detail in references 10 and 11. The accuracy of the temperature measurements in the AES and SEY experiment are estimated as  $\pm 3$  °C and  $\pm 10$  °C, respectively.

## 2.4 Static secondary ion mass spectroscopy (SSIMS)

SSIMS measurements are carried out in an ESCA 5400/SIMS 3600 multi-purpose system from Physical Electronics, which is equipped with a Balzers quadrupole mass spectrometer and an Ar<sup>+</sup> ion source.

Positive and negative secondary ion spectra are acquired using 5 nA of 2 keV Ar<sup>+</sup> ions, which are scanned over a surface area of 0.15 cm<sup>2</sup>. The acquisition time for one spectrum in the range 0 to 200 amu is about 60 s and hence the ion dose needed for the acquisition of one secondary ion spectrum is about  $1.5 \cdot 10^{13}$  ions cm<sup>-2</sup>. After each SSIMS measurement the sample position is changed to a new non irradiated surface area.

An XPS analysis of the surface before and after the acquisition of one secondary ion spectrum did not show any changes of the photoelectron peaks and it is therefore assumed that the ion dose of  $1.5 \cdot 10^{13}$  ions cm<sup>-2</sup> is within the static limit for SIMS measurements.

### 3. RESULTS

#### 3.1 SEY evolution with heating temperature and heating time at a constant temperature of 150 °C

The SEY versus PE curves for the as-received Nb thin film as a function of heating temperature are shown in Figure 2. Each temperature was kept constant for 1 h and immediately after the 1 h heating the SEY was measured, i.e. the sample was hot during the SEY measurements.

The maximum SEY ( $\delta_{max}$ ) of atomically clean Nb is  $\delta_{max} = 1.2$  and the primary electron energy  $E_{max}$  at which the maximum yield is obtained is  $E_{max} = 375$  eV [4]. During the air exposure following the deposition of the Nb thin film the maximum SEY value of the as-received Nb surface increases to 1.7 at  $E_{max} = 300$  eV.

During subsequent heat treatment, the SEY decreases continuously with increasing heating temperature. A significant SEY reduction is already observed after the 120 °C heat treatment and after 1 h heating at 200 °C the maximum SEY is reduced from 1.7 to 1.3. After 1 h 300 °C heating the maximum SEY value of the Nb thin film is about 1.1 and the peak maximum position shifts to  $E_{max} = 350$  eV. After the 350 °C measurement the sample was cooled down to room temperature (cool down time about 6 hours) and the SEY was measured again. The SEY values that were measured after cooling to room temperature varied less than 0.05 from those measured directly at the end of the 350 °C heating.

In the right plot of Figure 2 the SEY variation as a function of heating time at a constant temperature of 150 °C is shown. The maximum SEY of the Nb thin film decreases during the first 10 min of 150 °C heating from 1.7 to 1.5 and with increasing heating time the SEY continues to decrease slightly. After 4 hours 150 °C heating the maximum SEY is 1.4 and does not decrease further with increasing heating time.

#### 3.2 The variation of the surface composition as a function of heating temperature as observed by AES

The evolution of the elemental surface composition on the Nb thin film during the thermal cycle described above has been determined by AES. The Auger electron spectra that are acquired in the as-received state and after 1 h *in-situ* heating at different temperatures are shown in Figure 3.

In the as-received Auger electron spectrum C, O, N and Nb are detected. Characteristic changes occur in the AES spectra only after heating at 250 °C. These changes include an O-KLL signal depletion and Nb-MNV peak shape changes [12], both indicating the reduction of the native Nb oxide. The oxide reduction is accompanied by C-KLL peak shape variations [13] that indicate the transformation of adsorbed hydrocarbons into carbides. Because of the C-KLL peak shape changes the peak-to-peak height can not be used for a comparison of the carbon peak intensities after the different heat treatments [14].

#### 3.3 The variation of the surface composition as a function of heating temperature as observed by SSIMS

The positive secondary ion mass spectra of the Nb thin film in the as-received state and after *in-situ* heating at various temperatures are shown in the atomic mass unit (amu) range from 0 to 140 in Figure 4 and Figure 5, respectively. The amu range 0 to 50 of these spectra is plotted in more detail in Figure 6 in order to highlight temperature dependent variations of the low mass range.

The peaks at lower masses in the positive ion spectrum are mainly caused by molecular hydrocarbon fragments (e.g. 15-CH<sub>3</sub>, 27-C<sub>2</sub>H<sub>3</sub>, 29-C<sub>2</sub>H<sub>5</sub>, 41-C<sub>3</sub>H<sub>5</sub>, 43-C<sub>3</sub>H<sub>7</sub>). After heating at 160 °C the intensities of the hydrocarbon peaks are reduced with respect to the Nb metal and oxide peaks (see Figure 5), while the peak pattern in the low amu region is only weakly affected by the 160 °C heat treatment. Strong changes in the low amu region are only observed after 250 °C heating.

## 4. DISCUSSION

### 4.1 The SEY of air exposed metal surfaces

The SEY of the atomically clean Nb thin film increases strongly during an air exposure lasting 2 h. A strong SEY increase during air exposure is also observed for all other initially atomically clean metals, for which the SEY has been measured at CERN (Cu [15], Al, Ti, TiZr, TiZrV [11] and stainless steel [16]).

In order to cause the important SEY variation during the air exposure of an initially clean surface, it is necessary to form either a high SEY surface layer that is so thick that an important fraction of the SE emitted is generated within this layer and/or to change significantly the SE escape probability.

The influence of the SE escape probability on the SEY: The  $E_{max}$  shift to lower primary electron energy during air exposures of atomically clean metal surfaces

Knowing the very strong effect which the escape probability, and in particular the work function of metals has on electron emission phenomena such as thermionic or field emission, changes of the SEY are often attributed to changes in the surface work function. However, from the considerations given below it can be excluded that the SEY increase during air exposure of metals is mainly caused by changes of the SE escape probability.

The “universal” shape of the SEY versus PE energy curves is determined by the SE escape depth and the average penetration depth of the PE in the metal. The SE escape depth is in metals typically in the order of 3 – 5 nm [17]. In the energy range of interest for SEY measurements the PE penetration depth varies approximately with  $E_{PE}^{3/2}$  [18]. With increasing PE energy more SE are generated but the average depth in which the SE are generated increases. The maximum yield in the SEY spectrum is obtained when the PE deposit a maximum energy within the depth from which the SE can be emitted into the vacuum.

If the SE escape probability is increased,  $\delta_{max}$  increases and  $E_{max}$  shifts to higher PE energy because SE that are produced deeper in the bulk, having in the average a lower kinetic energy when they reach the surface, can now escape into the vacuum. This is for instance observed when the work function of sputter-cleaned copper is drastically reduced during the adsorption of sub-monolayer quantities of alkali metals [19].

However, when pure metals are exposed to air an increase of the SEY is usually accompanied by a shift of  $E_{max}$  to lower PE energy.  $E_{max}$  of sputter-cleaned copper, as an example, is shifted from 650 eV to less than 400 eV during air exposure [5]. In the case of Nb the shift of  $E_{max}$  to lower PE energy during air exposures is also observed ( $E_{max,Nb,air-exposed} = 300$  eV) but it is less pronounced because  $E_{max}$  of pure Nb metal is already comparatively low ( $E_{max,Nb} = 375$  eV instead of  $E_{max,Cu} = 650$  eV).

It can therefore be concluded that the enhancement of SE emission during the air exposure is not mainly caused by an increased escape probability because otherwise  $E_{max}$  would shift to higher PE energies instead of the observed shift to lower energies. Hence, the

surface layer formed during an air exposure must have a higher SEY than the underlying metal and an important fraction of all SE emitted must be generated within this layer.

#### **4.1.1 *The surface composition of air exposed metal surfaces***

Atomically clean metal surfaces have a high surface free energy. If such surfaces are exposed to the ambient air a series of processes take place, successively reducing the surface free energy.

Typically 2-3 nm of oxide are formed at room temperature in air, reducing the surface free energy to a few  $100 \text{ mJ m}^{-2}$ . Subsequent exposure to humid air leads to a transformation of the outermost metal oxides into hydroxides [20]. On top of the hydroxides a thin layer of  $\text{H}_2\text{O}$  is adsorbed, its free surface energy being approximately  $70 \text{ mJ m}^{-2}$ .

After the virtually instantaneous oxidation in ambient air, organic contamination is adsorbed above the inorganic phase in a dynamic process, which can continue for many days. XPS measurements show that the organic contamination can grow to a thickness similar to that of the underlying oxide [21]. Water molecules can be bound within the organic phase via hydrogen bonds and an amount corresponding to several monolayers of water, extending through the entire organic phase can be adsorbed during exposure to humid air.

#### **4.1.2 *The SEY of the air formed metal oxides***

The SEY increase during ambient air exposure of metals is often attributed to the formation of the surface oxides. This is however only true in some cases since many native metal oxides have lower SEY values than the corresponding parent metals.

Compared to metals the SEY of insulators is very high, mainly because of the large SE escape depth in insulating materials [4]. One example for such metals is Al, which native oxide  $\text{Al}_2\text{O}_3$  has insulating properties and a high SEY. The SEY of technological Al surfaces is therefore particularly high, despite the low  $\delta_{max}$  value of 1.0 for atomically clean Al.

On the other hand the SEY of semiconducting metal oxides is often lower than that of the parent metals. The native Cu oxide  $\text{Cu}_2\text{O}$ , as an example, is semiconducting and has a lower SEY than atomically clean Cu [5]. Also  $\text{Nb}_2\text{O}_5$ , the native Nb oxide that is mainly formed during air exposures at ambient temperature, has a lower SEY than that of atomically clean Nb [22]. Hence, the  $\delta_{max}$  increase from 1.2, which is the value for atomically clean Nb [4], to 1.7 can not be attributed to the Nb surface oxidation in ambient air.

#### **4.1.3 *The SEY of the organic surface contamination***

In the following it is assumed that the organic surface contamination which is adsorbed during air exposures is similar on the different metal oxides. Water molecules embedded in the organic layer are here considered as being a part of the organic contamination.

The thickness of the organic surface contamination that is adsorbed even during long lasting air exposures is thinner than the SE escape depth. Thus, the SEY of this contamination layer can not be measured directly because the obtained SEY values will always be influenced by the properties of the substrate.

However, the SEY of the surface contamination can be estimated by comparing SEY measurements of air exposed insulating materials and metals. While the SEY of

metals is increased the SEY of insulating materials is reduced during air exposures. As a result, *in-situ* cleaning of air exposed insulating oxides increases the SEY contrary to what is observed when *in-situ* cleaning air exposed metals. The SEY of alumina, as an example, increases from 5.7 in the as-received state to 8.2 after a 250 °C bakeout [23]. From this one can conclude that the SEY of the surface contamination is higher than that of metals but lower than that of typical insulating materials.

The SEY of materials which maximum SEY is about 3 is only slightly effected by air exposures and therefore the authors of reference 23 conclude that the maximum SEY of the airborne contamination layer is about 3.

Assuming that a surface layer with a maximum SEY of about 3 is adsorbed on all metals during air exposures one can generally expect an air exposure induced SEY increase because maximum SEY values of pure metals vary between 0.6 and 1.7 [4].

#### 4.1.4 *The SEY of pure water*

Water, which is adsorbed from humid air and trapped within the organic contaminants, can contribute to the SEY increase. The thicker the organic contamination layer, the more water can be embedded within it [21].  $\delta_{max}$  of a thick H<sub>2</sub>O layer condensed at 77 K has been measured as about 2.3 with an  $E_{max}$  of about 280 eV [16].

Pure water exposure in vacuum at room temperature increases the SEY of atomically clean Cu only slightly [5]. This can be explained by the fact that the water layer, which is adsorbed on clean metals in a pure water atmosphere, is so thin that only a small amount of SE is generated within this layer.

## 4.2 **The reasons for the SEY reduction during thermal treatments**

Like the general SEY increase of metals during air exposures one observes also a general decrease of the SEY when these surfaces are heated during a bake-out under vacuum. The maximum SEY of the air exposed Nb thin film is strongly reduced from 1.7 to about 1.3 during a 1 h heat treatment at 160 °C. At the same time the secondary ion mass peak pattern of the hydrocarbon contamination is almost unchanged in the 160 °C spectrum compared to that of the as-received spectrum, indicating that the surface chemistry is not significantly changed.

However, the intensity of the hydrocarbon peaks relative to the intensity of metal and metal oxide peaks (see Figure 5) is strongly reduced after the 1 h 160 °C heat treatment. Assuming that this ratio is only weakly influenced by matrix effects this indicates that a part of the hydrocarbon contamination is removed during the heat treatment and the SEY decrease during heat treatments may therefore be attributable to a thinning of the contamination layer on top of the Nb-oxide. The thermal desorption of H<sub>2</sub>O during the 160 °C heat treatment may also contribute to the SEY decrease.

Because of the severe electron beam damage that occurs during the acquisition of an Auger spectrum the removal of weakly bound species during the 160 °C heating is not revealed by the AES measurements.

The surface cleaning during a bake-out can occur through thermal desorption and/or through diffusion of contaminants into the metal bulk [24]. The latter case is exploited for *in-situ* cleaning (activation) of bulk getters, so-called non-evaporable getters (NEG) [11].

Characteristic changes [10] in the Auger electron spectra in Figure 3 (O-KLL intensity depletion, Nb-MNV and C-KLL peak shape changes) indicate that at 250 °C the

surface oxide layer starts to diffuse into the Nb bulk, i.e. Nb can act as a NEG. This is consistent with AES depth profiling measurements [25] showing that the oxide of the Nb<sub>2</sub>O<sub>5</sub>/Nb system is dissolved into the Nb bulk when heated to 325 °C while at 150 °C no oxide dissolution occurs.

In a previous study of TiZr and TiZrV NEG coatings [11] a correlation has been found between the NEG activation temperature and the temperature needed to decrease the SEY to values close to those of the clean metals.

In the present case of the Nb thin film only 1 h heating at 160 °C is sufficient to reduce its maximum SEY to about 1.4. However, heating temperatures above 250 °C are needed to decrease the SEY of chemically cleaned bulk Nb to the same value [8].

#### **4.2.1 The SEY of the activated Nb thin film**

The SEY of the fully activated Nb thin film (after 1 h heating at 350 °C) is below that of atomically clean Nb. AES results show that after the 350 °C treatment the Nb samples are not atomically clean with O and C present on the sample surface. The C-KLL peak shape in the Auger spectra is characteristic for carbide.

In a previous study for both NbC and Nb<sub>2</sub>O<sub>5</sub> SEY values below those of pure Nb have been reported [22]. The low SEY of the fully activated Nb thin film might thus be explained by the low SEY of the Nb oxide and carbide present on the surface.

#### **4.2.2 The influence of chemical cleaning procedures on the SEY of metals**

$\delta_{max}$  of a freshly deposited Nb thin film increases during a 2 h air exposure to a value of 1.7, which is much below the  $\delta_{max}$  value of 2.2, reported for chemically polished Nb [8]. Also for copper it has been found that after an identical air exposure time the SEY of chemically cleaned copper is much higher than the SEY of a copper surface that was sputter-cleaned before the air exposure [5].

This difference in the SEY can be ascribed to the thickness and the nature of the contamination layer that is formed either after air exposure or after chemical treatment plus air exposure. On chemically treated surfaces the contamination layer is usually thicker than that formed during air exposure of atomically clean surfaces. In some cases the low SEY of so-called “magic” surface coatings may therefore be attributable to the fact that these do not need to be chemically cleaned while the SEY of the coating material may be of minor importance.

The sample preparation has also a strong effect on the efficiency of thermal treatments for reducing the SEY. For air exposed Nb and Cu a 350 °C bake-out decreases the SEY to values below those of the atomically clean metals, provided that the metal was clean before the air exposure. *Ex situ* cleaning, e.g. by sputter etching, is therefore advantageous for obtaining low SEY surfaces after consecutive *in situ* bakeouts.

## **5. CONCLUSION**

The SEY of air exposed metal surfaces is generally higher than the SEY of the corresponding atomically clean metals.

The SEY increase during air exposures is mainly caused by the adsorption of an organic surface contamination with embedded water molecules. In some cases the formation of an insulating oxide or hydroxide can contribute to the overall SEY increase.



The SEY of air exposed metal surfaces is related to the degree of surface contamination. The stronger the contamination the higher is the SEY. After chemical cleaning treatments the contamination layer is usually thicker than it is after air exposure of initially atomically clean samples. Therefore, the SEY of an air exposed Nb thin film is lower than that of a chemically polished Nb surface.

The SEY of air exposed metals decreases during *in-situ* heat treatments. The cleaner the initial surface state, the lower is the temperature needed to decrease the SEY to a certain value. In the case of NEG the temperature at which the SEY is effectively reduced can be particularly low.

### **Acknowledgements**

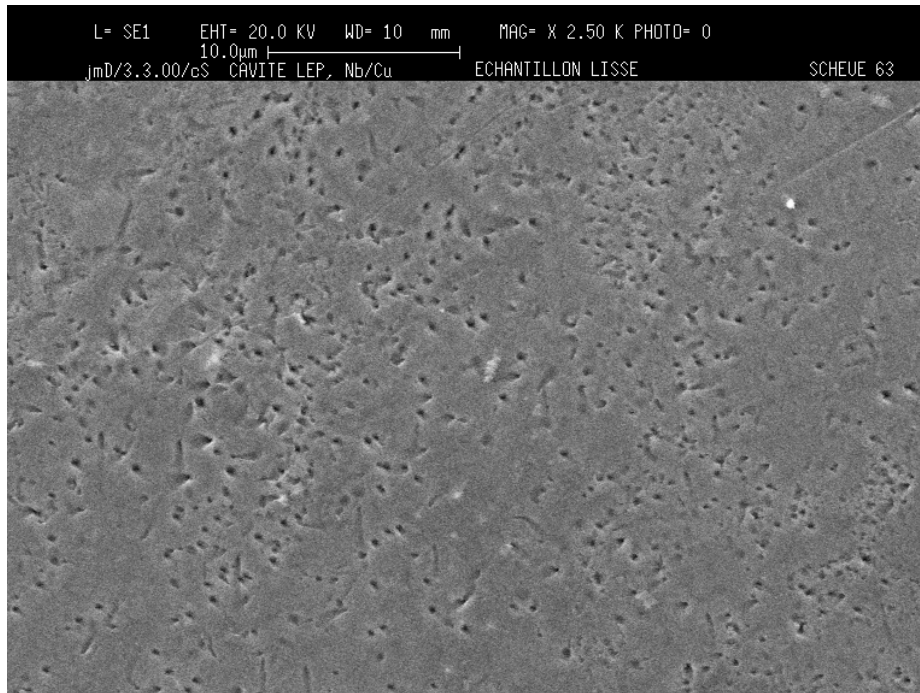
We would like to thank A. Van't Hof for the preparation of the samples and J.-M. Dalin for the SEM images. To S. Calatroni we are grateful for a critical reading of the manuscript.

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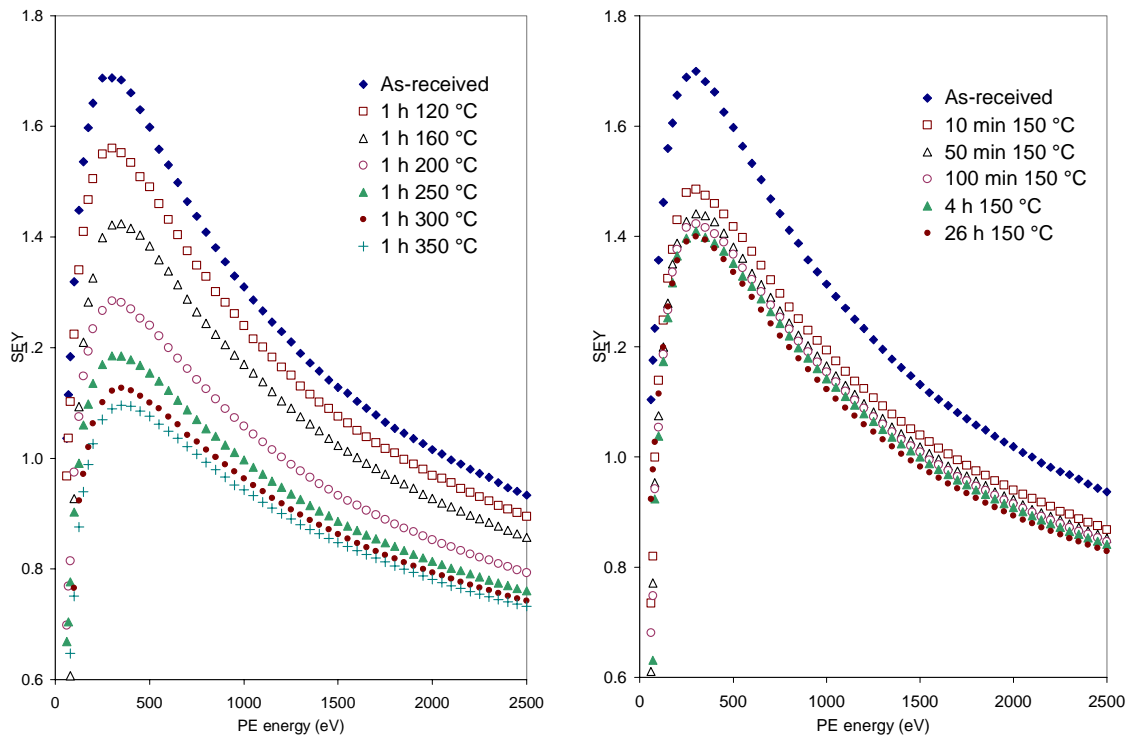
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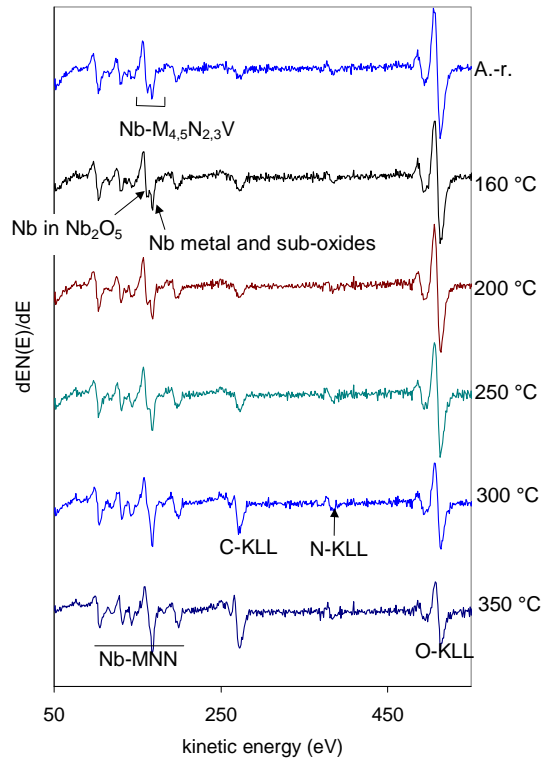
## Figures



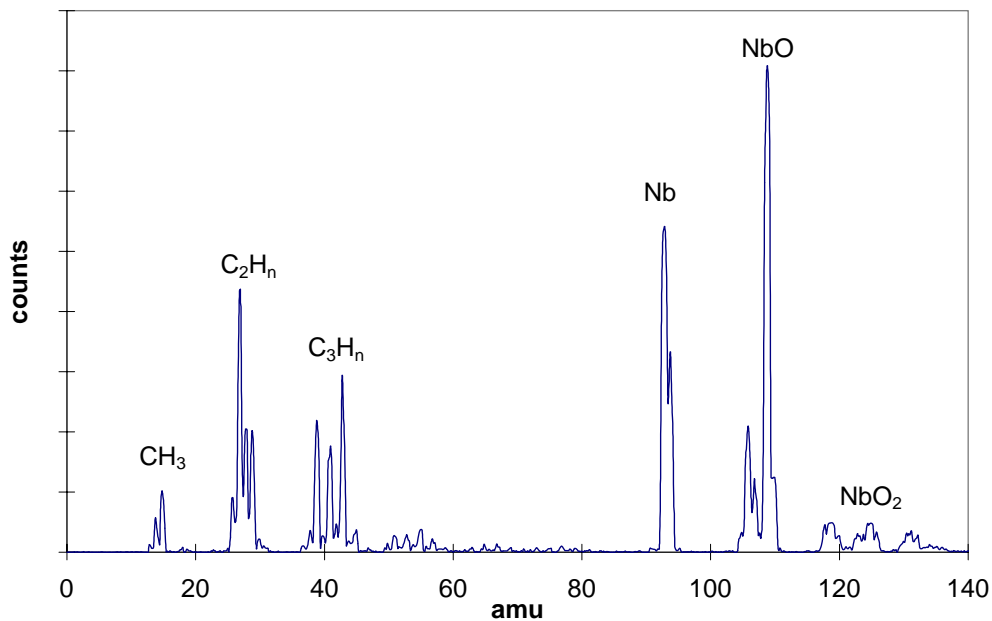
**Figure 1:** Secondary electron image of a Nb thin film, 1.5  $\mu\text{m}$  thick sputter-deposited onto a chemically polished copper substrate.



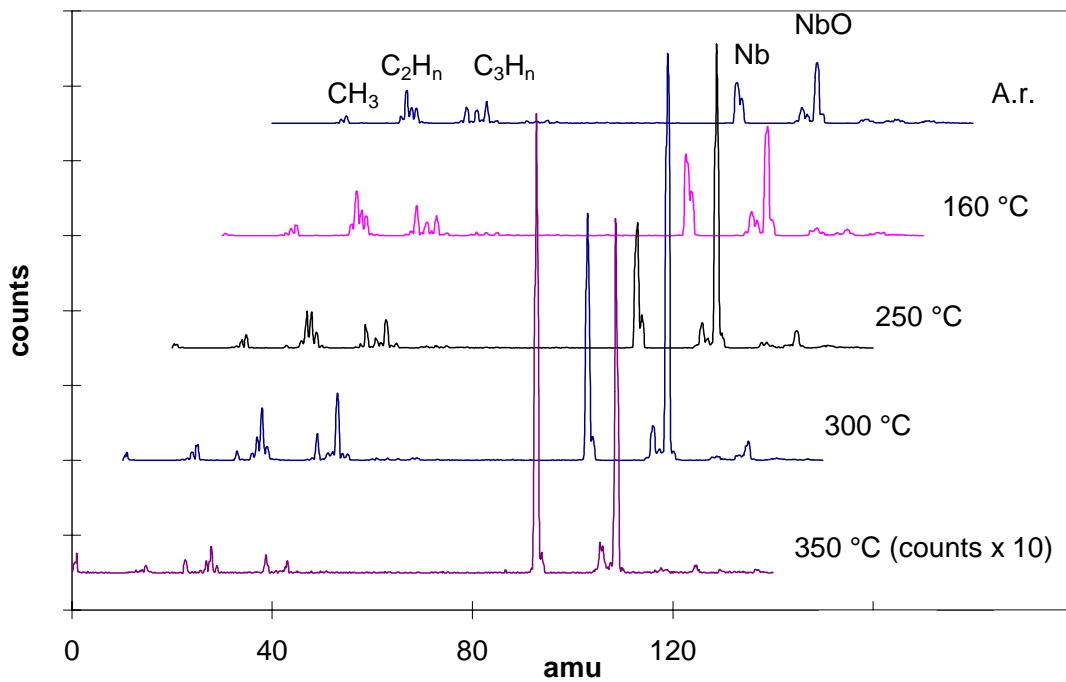
**Figure 2:** SEY versus PE energy of a Nb thin film as a function of heating temperature at 1 h heating time (left plot) and as a function of heating time at 150 °C (right plot).



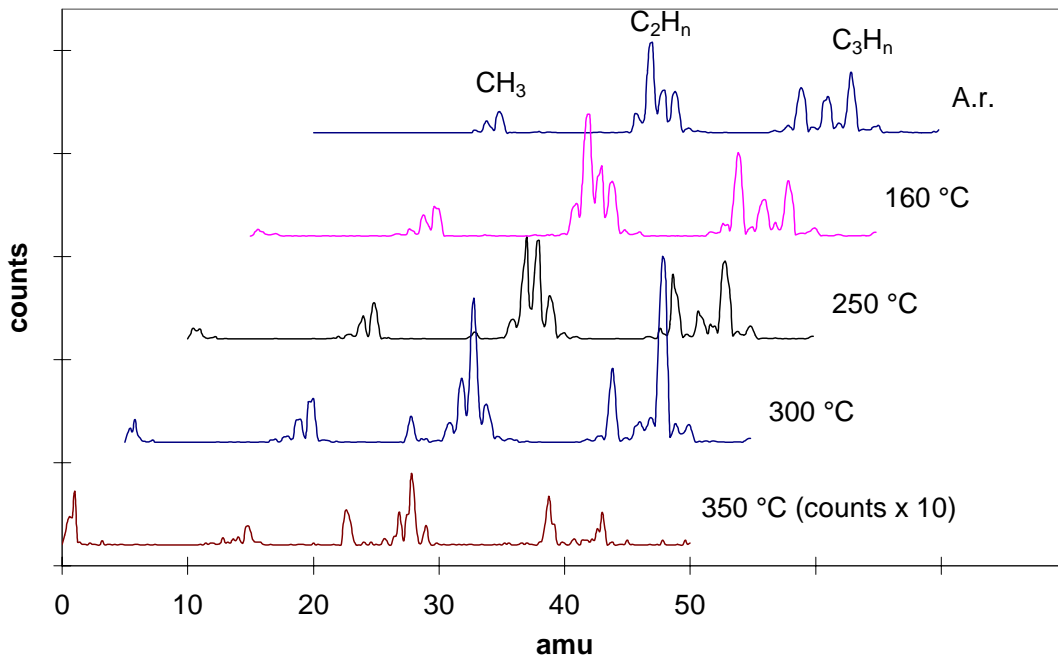
**Figure 3:** Derivative dEN(E)/dE Auger electron spectra of Nb thin film, as-received (A.-r.) and after 1 hour heating at 160, 200, 250, 300 and 350 °C. An O-KLL intensity depletion and Nb-MNV peak shape changes indicate the onset of the reduction of Nb<sub>2</sub>O<sub>5</sub> at 250 °C. At 300 °C the transformation of adsorbed hydrocarbons into carbides is indicated by C-KLL peak shape changes.



**Figure 4:** Positive secondary ion mass spectra of Nb thin film as-received (A.r.). The peaks at 93, 109 and 125 amu are characteristic for Nb<sup>+</sup>, NbO<sup>+</sup> and NbO<sub>2</sub><sup>+</sup>, respectively. The peaks at 15, 27, 29, 41 and 43 amu are from hydrocarbon species.



**Figure 5:** Positive secondary ion mass spectra of Nb thin film as-received (A.r.) and after 1 h heating at different temperatures. The peaks at 93, 109 and 125 amu are characteristic for Nb<sup>+</sup>, NbO<sup>+</sup> and NbO<sub>2</sub><sup>+</sup>, respectively. The spectrum acquired after the 350 °C heat treatment is multiplied by a factor of 10. The reduction of the Nb oxide during the 350 °C treatment is indicated by a variation of the Nb/NbO peak intensity ratio.



**Figure 6:** Positive secondary ion mass spectra of a Nb thin film as-received (A.r.) and after 1 h heating at different temperatures. The plot shows the spectra of Figure 5 in the range (0-50) amu. The 350 °C spectrum is multiplied by a factor of 10.