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**An AES Study of the Room Temperature Surface
Conditioning of Technological Metal Surfaces
by Electron Irradiation**

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Abstract

The modifications to technological copper and niobium surfaces induced by 2.5 keV electron irradiation have been investigated in the context of the conditioning process occurring in particle accelerator ultra high vacuum systems. Changes in the elemental surface composition have been found using Scanning Auger Microscopy (SAM) by monitoring the carbon, oxygen and metal Auger peak intensities as a function of electron irradiation in the dose range 10^{-6} to 10^{-2} C mm⁻². The surface analysis results are compared with electron dose dependent secondary electron and electron stimulated desorption yield measurements.

Initially the electron irradiation causes a surface cleaning through electron stimulated desorption, in particular of hydrogen. During this period both the electron stimulated desorption and secondary electron yield decrease as a function of electron dose. When the electron dose exceeds 10^{-4} C mm⁻² electron stimulated desorption yields are reduced by several orders of magnitude and the electron beam induced growth of a carbon layer becomes the dominant process. Simultaneously the secondary electron yield is further reduced to values which are below those of an atomically clean metal surface.

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1. INTRODUCTION

The internal walls of the ultra high vacuum (UHV) system of particle accelerators are subjected to synchrotron radiation and energetic electron and ion irradiation, which affect the functional surface properties of the wall such as the secondary electron yield (SEY) and the electron stimulated desorption (ESD) yield. This process is usually advantageous for the operation of particle accelerators and it is called surface conditioning or beam scrubbing [1].

The design luminosity of CERN's next accelerator, the Large Hadron Collider (LHC) [2], can only be achieved if the SEY of the beam vacuum walls in the LHC arcs is strongly reduced by surface conditioning during the initial LHC operation [3]. An understanding of the conditioning process may therefore help to make predictions on the conditioning time required to reach the LHC design parameters.

Surface conditioning can be studied in different ways, for instance by measuring the electron dose dependence of the SEY and the ESD yield. Already after a low electron exposure of about 10^{-6} C mm⁻² the SEY of technological metal surfaces starts to decrease strongly, reaching its lowest value after about 10^{-2} C mm⁻² [4]. The SEY reduction during electron irradiation is also observed in a scanning electron microscope as a contrast in secondary electron images, which appears when changing from high to low magnification. ESD yields are reduced by several orders of magnitude during the first 10^{-3} C mm⁻² of electron exposure [5,6].

Electron beam induced surface modifications are also known to cause artefacts in Auger electron spectroscopy (AES), referred to as beam damage. A comprehensive review of electron beam damage in AES is given in reference [7]. The electron dose at which beam damage is observed in the Auger electron spectra depends on the material analysed. On condensed layers of (CH₃)₂O, CH₃OH and H₂O, for example, electron beam damage has been reported to occur after electron doses as low as $5 \cdot 10^{-6}$ C mm⁻² [8].

In a previous publication [9] we have described the electron beam induced surface variations, and in particular the electron stimulated deposition of carbon on surfaces used in accelerator UHV systems, notably chemically degreased copper and a TiZrV non-evaporable getter thin film. The influence of 2.5 keV electron irradiation was investigated by AES in the electron dose range (10^{-3} to 1) C mm⁻². Measurements with lower electron doses were not possible with the instrument used.

The aim of the present study is to monitor the surface variations during continuous electron irradiation in the range (10^{-6} to 10^{-2} C) mm⁻², in order to better understand the surface modifications causing the SEY decrease during the conditioning process in accelerator vacuum systems. Niobium and copper have been chosen as sample materials because their surface conditioning is of great importance for the performance of particle accelerators. Niobium is used in superconducting RF cavities [10] and copper will be used as the internal surface of the cold UHV system of CERN's next accelerator, the Large Hadron Collider (LHC).

2. EXPERIMENTAL

2.1 The samples

Two different samples have been investigated:

- 1) Oxygen-free electrolyte (OFE) bulk copper, chemically degreased in an ultrasonic bath of an alkaline solution (No. 17.40 from NGL Cleaning

Technology), rinsed by immersion in an ultrasonic cold demineralised water bath (conductivity $< 5 \mu\text{S cm}^{-1}$) and dried at 80°C in filtered air.

- 2) A Niobium thin film, about $1.5 \mu\text{m}$ thick, sputter deposited onto a chemically polished OFE copper substrate. Such films are produced at CERN as superconducting coatings, which are deposited onto the internal walls of copper cavities for particle acceleration [11].

2.2 Auger electron spectroscopy (AES)

AES measurements are performed with a VG Scientific MICROLAB mk.II scanning Auger microscope (SAM). The electron spectrometer is a hemispherical sector analyser, which was operated with a constant retard ratio of four.

The experimental UHV system is pumped by an oil diffusion pump in combination with a liquid nitrogen cooled cold trap, a titanium sublimation pump and a sputter ion pump. The total pressure reading during the experiments is about $3 \cdot 10^{-8}$ Pa (N_2 equivalent).

The electron source is a Schottky field emission source YEO3/VGMLAB from York Electron Optics Ltd.. The electron beam energy was 2.5 keV and the specimen current was about 5 nA (measured with a sample bias of $+18 \text{ V}$) at a beam energy of 2.5 keV .

The surface area irradiated by the electron beam has been measured using a calibrated standard sample. Initially this area was $0.52 \times 0.6 \text{ mm}^2$. In order to investigate an electron dose range over almost four orders of magnitude in a reasonable time, electron irradiation was performed at three different magnifications. After an electron exposure of approximately $10^{-5} \text{ C mm}^{-2}$ the irradiated surface area was reduced by a factor of four, and after $10^{-4} \text{ C mm}^{-2}$ again by a factor of four, by increasing the magnification.

Auger electron spectra are acquired and evaluated in the direct N(E) mode. This is necessary as for very low electron doses, Auger spectra in the derivative mode do not yield a sufficiently high signal-to-noise ratio for peak intensity measurements. In addition possible peak shape changes could cause errors in the C-KLL peak-to-peak height measurement from the derivative spectra [9]. The peak intensity is measured as the peak area after the subtraction of a linear background. Before measuring the intensity, the N(E) spectra are smoothed by a moving average over 9 eV and the background intensity of all spectra is normalised at 600 eV .

Auger spectra in the kinetic energy range (30 to 1000) eV are acquired with a 1 eV step and a dwell time of 100 ms/step . Hence, the minimum electron dose to which a surface is exposed during the acquisition of one Auger spectrum is about $2 \cdot 10^{-6} \text{ C mm}^{-2}$ (with an electron current of 5 nA and an irradiated surface area of 0.3 mm^2).

2.3 The SEY at 2.5 keV as a function of electron dose

The variation of the secondary electron yield (SEY) at 2.5 keV primary electron (PE) energy with increasing electron dose is estimated using equation (1). The SEY value is calculated from the PE beam current, measured with $+18 \text{ V}$ sample bias, and the sample-to-ground current, measured with a sample bias of -18 V .

$$\text{SEY}_{2.5 \text{ keV}} = (\text{I}_{\text{beam}} - \text{I}_{\text{sample}}) / \text{I}_{\text{beam}} \quad (1)$$

No attempt has been made to optimise the bias voltages and the calculated SEY values are used to show trends but do not correspond to true SEY values.

3. RESULTS

3.1 Surface variations on chemically cleaned copper as observed by AES

The direct N(E) Auger electron spectra of a chemically cleaned copper sample as a function of electron dose are shown in Figure 1. The corresponding carbon, oxygen and copper peak intensity evolution is plotted in Figure 2.

The carbon peak intensity decreases until an electron dose of about 10^{-4} C mm⁻² is reached. With higher electron doses the carbon peak intensity increases. The copper Auger peak intensity shows the opposite trend, i.e. up to 10^{-4} C mm⁻² it increases almost by a factor of two and starts then to decrease at higher electron doses.

During the electron irradiation the position of the carbon Auger peak maximum shifts by about 5 eV to a higher kinetic energy (see Figure 3) while the position of the oxygen and copper Auger peaks remain unaffected.

3.2 Niobium thin film

The N(E) spectra of an air exposed Nb thin film are plotted in Figure 4 as a function of electron dose. The corresponding carbon, oxygen and niobium peak intensity evolution as a function of electron dose is plotted in Figure 5.

As for copper, the carbon peak intensity on niobium reaches a minimum value after about 10^{-4} C mm⁻² and starts then to increase again with higher electron doses. The niobium Auger peak intensity increases continuously up to $4 \cdot 10^{-3}$ C mm⁻², which is the maximum electron dose applied to the niobium sample. The oxygen peak intensity increases slightly and then remains almost constant with higher doses. The C-KLL peak shifts to higher energies. An electron exposure of $2 \cdot 10^{-4}$ C mm⁻² causes a small peak shift of about 1 eV and after a dose of $4 \cdot 10^{-3}$ C mm⁻² the C-KLL peak is shifted by about 5 eV to higher kinetic energy.

3.3 The variation of the SEY at 2.5 keV PE energy

When reducing the magnification of the SAM by rastering the electron beam over a larger surface area a contrast between the newly and previously irradiated area is observable even after an electron dose of less than 10^{-5} C mm⁻². The small area, which is exposed to a higher electron dose, appears darker than the larger area, indicating that the SEY decreases with increasing electron dose.

In Figure 6 the SEY values calculated using Equation (1) are plotted as a function of electron dose. On both substrate materials the SEY values decrease with the electron dose with an approximately logarithmic rate. After an exposure in the order of 10^{-3} C mm⁻² the rate with which the SEY is reduced slows down.

4. DISCUSSION

4.1 The variation of the C-KLL peak intensity as a function of electron dose

During the first 10^{-4} C mm⁻² electron irradiation the C-KLL peak intensity on the Cu and Nb sample is reduced by about 30 %. With higher electron doses the C-KLL intensity starts to increase. This behaviour can be understood as a simultaneous carbon desorption and deposition process, taking into account the different kinetics for both processes.

The removal of carbon via ESD is initially the dominant process but ESD yields decrease drastically with increasing electron dose. ESD measurements on chemically cleaned copper, which are carried out at 300 eV PE energy, show that ESD yields for CO₂, CO, CH₄ and C₂H₆ are initially between $5 \cdot 10^{-2}$ and $5 \cdot 10^{-1}$ molecules per PE [6]. On increasing the electron dose from (10^{-7} to 10^{-4}) C mm⁻² these ESD yield values are reduced by about 2 orders of magnitude and a dose of 10^{-3} C mm⁻² decreases the ESD yield values by an additional order of magnitude.

Electron doses higher than 10^{-4} C mm⁻² cause an increase in the carbon peak intensity, indicating the growth of a carbonaceous surface layer. This phenomenon has already been described in a previous publication [9], where it was demonstrated that in the range (10^{-3} – 1) C mm⁻² the C-*KLL* peak intensity increase on OFE copper is proportional to the electron dose. This indicates that the carbonaceous layer grows with a constant rate. Hence, the carbon surface coverage is reduced until desorption and deposition rates are equal and higher electron doses cause a net increase of the carbon surface coverage.

During electron irradiation the carbon Auger peak position shifts on both substrates by about 5 eV to higher kinetic energy, suggesting a change in the chemical state of carbon. This may be associated with the transformation of hydrocarbon species to amorphous carbon through the loss of hydrogen. More information about these chemical state variations could be obtained by surface analysis techniques which have a higher chemical specificity than AES, notably high resolution X-ray photoelectron spectroscopy (XPS) or static secondary ion mass spectroscopy (SSIMS) measurements.

4.2 The variation of the metal peak intensity as a function of electron dose

The most notable variation in the Auger spectra caused by the PE irradiation is the strong increase of the metal peak intensities. After about 10^{-4} C mm⁻², the Cu and Nb peak intensities increase by approximately 100 % and 50 %, respectively. This indicates an effective electron irradiation induced surface cleaning. The electron current density is so low that sample heating can be neglected [12] and hence the surface cleaning occurs via electron stimulated desorption.

From ESD measurements it is known that hydrogen is the main gas which is desorbed under electron impact (the ESD value reported in reference 6 for chemically cleaned copper is two H₂ molecules per 300 eV PE [6]). It is therefore assumed that the metal peak increase is mainly an indirect evidence for surface cleaning through the desorption of hydrogen (H atoms constitute a significant fraction of the adsorbates omnipresent on an air exposed metal surfaces). The desorption of other species such as CO₂, CO, CH₄ and H₂O also contribute to the metal peak growth.

The dehydrogenation of the surface layer may also cause the C-*KLL* peak shape variations indicating chemical state changes of adsorbed hydrocarbons. Various studies on the electron irradiation induced surface variations on different hydrocarbon layers [13,14,15] have been carried out using different techniques. These investigations confirm that the main effect of the electron irradiation is the dehydrogenation of the hydrocarbon molecules through dissociative electron attachment.

4.3 The variation of the O-KLL peak intensity as a function of electron dose

Oxygen Auger peak intensity changes are less pronounced than those of the carbon and metal peaks. This may seem surprising since ESD measurements predict that a significant quantity of CO₂ and CO is desorbed. However, oxygen is not only present in the surface contamination layer but also in the underlying metal oxide layer. Hence, the reduction of the

oxygen signal from the contamination layer by ESD can be compensated by an increase of the oxygen signal from the underlying oxide layer, which is less attenuated as the surface is progressively cleaned.

4.4 Electron beam damage in the AES analysis of air exposed metal surfaces

The measurements presented show that on air exposed metal surfaces an electron beam induced damage occurs even at electron doses below $10^{-5} \text{ C mm}^{-2}$. SEY measurements as a function of the electron dose show a significant SEY reduction already after $10^{-6} \text{ C mm}^{-2}$ [4]. Therefore, one can expect that even during the acquisition of the first spectrum with the very low dose of $2 \cdot 10^{-6} \text{ C mm}^{-2}$ the surface is significantly modified by the electron beam. This electron beam damage mainly consists in the removal of hydrogen, which manifests itself indirectly by a strong increase of the substrate metal peak areas.

Electron beam damage will result in a time-dependent instrumental artefact when undertaking quantitative analyses. For example, relative carbon concentrations (based on a relatively crude homogeneous distribution model) are often used to assess the degree of surface contamination by hydrocarbons [16]. In the present example of chemically degreased copper, the relative atomic carbon concentration, calculated using peak areas and sensitivity factors ($S_{C-KLL} = 1$, $S_{O-KLL} = 0.25$ and $S_{Cu-LMM} = 0.5$) would change from 36 at.% to 22 at.% after electron doses of $2 \cdot 10^{-6}$ and $2 \cdot 10^{-4} \text{ C mm}^{-2}$, respectively.

4.5 The reduction of the SEY during the conditioning of accelerator UHV systems and the electron beam induced contrast in scanning electron microscopy (SEM)

The conditioning process in accelerator UHV systems up to an electron dose of $10^{-4} \text{ C mm}^{-2}$ is expected to be mainly due to an electron induced surface cleaning. Other *in-situ* cleaning methods, such as heat treatments or sputter-etching, are also effective in reducing the SEY of technological metal surfaces. As an example, a 350 °C bakeout of technological OFE copper reduces the maximum SEY to about 1.4, which is only slightly higher than the SEY of pure copper [17]. A similar maximum SEY is obtained when the surface contamination is entirely removed from the copper surface by sputter-etching with $10^{18} \text{ Ar}^+ \text{ ions cm}^{-2}$ during a glow discharge.

When the electron dose exceeds $10^{-4} \text{ C mm}^{-2}$ desorption rates are strongly reduced and the growth rate of a carbonaceous contamination layer becomes dominant, causing a further SEY reduction. Electron dose dependent SEY measurements show that the SEY of technological copper as well as that of sputter-cleaned copper can be reduced to values below those of atomically clean copper when exposed to $10^{-2} \text{ C mm}^{-2}$ [4]. When such a low SEY surface is etched away by sputtering the SEY increases again to the values of atomically clean copper. This indicates that the very low SEY obtainable by exposing metals to electron doses exceeding $10^{-3} \text{ C mm}^{-2}$, is the result of a carbonaceous contamination growth.

It has been shown that on copper the electron induced carbon growth rate is independent of the CO , CO_2 and CH_4 partial pressures [9]. The mechanism by which this carbon contamination gets on the metal surface is subject of further investigation at CERN.

From AES measurements it can not be excluded that the carbon accumulation is an instrumental artefact, possibly caused by the adsorption of carbon containing radicals produced in the electron source. However, the SEY decrease of technological copper to values below those of atomically clean copper has not only been observed in laboratory systems using electron guns as an electron source, but also by *in-situ* SEY measurements in the UHV system of the Electron Positron Accumulator ring (EPA) at CERN [4].

Usually it is assumed that the contrast, which is observed when making a series of SEM images from high to low magnification, is caused by an electron beam induced deposition of carbonaceous species onto the irradiated surface area. However, the electron beam induced contrast in secondary electron images of technological metal surfaces is rather related to the surface cleaning via ESD and does not require the deposition of contaminants, since the electron dose needed for the acquisition of a secondary electron image is comparatively low (typically 10^{-5} C mm⁻² for the acquisition of an image with a magnification of 10 000 [18]).

5. CONCLUSION

On technological metal surfaces, electron beam damage is observed in Auger electron spectra even at electron doses below 10^{-5} C mm⁻². This beam damage is attributed to electron induced surface cleaning, mainly as a result of electron stimulated desorption of hydrogen. The electron stimulated surface cleaning can cause an important artefact in electron excited AES measurements, e.g. when so-called relative atomic carbon concentrations are used for the assessment of surface cleanliness.

A strong SEY decrease up to 10^{-4} C mm⁻² is coincident with the electron induced surface cleaning and attributed to the part removal of contamination, which is omnipresent on the technological metal surfaces in accelerator UHV systems.

When electron doses exceed 10^{-4} C mm⁻² an electron stimulated accumulation of carbonaceous species on the surface is observed. This is accompanied by a further reduction in the SEY, to values substantially lower than those of a clean metal surface.

References

- 1 J.C. Billy, J.P. Bojon, B. Henrist, N. Hilleret, M. J. Jimenez, I. Laugier, P. Strubin, *Vacuum* **60**, (2001), 183-189
- 2 The LHC Study Group, “The Large Hadron Collider, Conceptual Design”, CERN/AC/95-05, (1995)
- 3 O. Gröbner, LHC Project Report **127**, CERN, (1997)
- 4 V. Baglin, I. Collins, B. Henrist, N. Hilleret, G. Vorlaufer, LHC Project Report **472**, CERN, (2001)
- 5 M. Andritschky, *Vacuum* **39**, (1989), 649-652
- 6 F. Billard, N. Hilleret, G. Vorlaufer, “Some results on the electron induced desorption yield of OFHC copper”, *Vacuum Technical Note* 00-32, CERN, (2000)
- 7 C.G. Pantano, T.E. Madey, *Appl. Surf. Sci.* **7** (1981), 115-141
- 8 P.H. Holloway, T.E. Madey, C.T. Campbell, R.R. Rye, J.E. Houston, *Surf. Sci.* **88**, (1979), 121-137
- 9 C. Scheuerlein, M. Taborrelli, *J. Vac. Sci. Technol. A* **20**(1), (2002), 93-101
- 10 H. Lengeler, in *CERN Accelerator School Fifth General Accelerator Physics Course* **2**, 791, edited by S. Turner, CERN, (1994)
- 11 V. Arbet-Engels, C. Benvenuti, S. Calatroni, P. Darriulat, M.A. Peck, A.M. Valente, C.A. Van't Hof, CERN-EST-2000-001-SM, (2000)
- 12 L.G. Pittaway, *Brit. J. Appl. Phys.* **15**, (1964), 967
- 13 P.Rowntree, P.-C. Dugal, D.Hunting, L.Sanche, *J.Phys.Chem.* **100**, (1996), 4546
- 14 C.Olsen, P.Rowntree, *J.Chem. Phys.* **108**, (1998), 3750
- 15 K.Seshadri, K.Froyd, A.N.Parikh, D.L.Allara, M.J.Lercel, H.G.Craighead, *J.Phys. Chem.* **100**, (1996), 15900
- 16 C. Benvenuti, G. Canil, P. Chiggiato, P. Collin, R. Cosso, J. Guérin, S. Ilie, D. Latorre, K.S. Neil, *Vacuum* **53**, (1999), 317-320
- 17 I. Bojko, N. Hilleret, C. Scheuerlein, *J. Vac. Sci. Technol. A* **18**(3), (2000), 972
- 18 E. Demm, “*Rasterelektronenmikroskopie in der Halbleitertechnik*”, in “*Praxis der Rasterelektronenmikroskopie*”, edited by P.F. Schmidt, Expert Verlag GmbH, Renningen, (1994)

Figure 1: Direct N(E) Auger electron spectra of chemically cleaned copper film acquired after an electron exposure of ($2 \cdot 10^{-6}$, $1 \cdot 10^{-5}$, $2 \cdot 10^{-4}$, $1 \cdot 10^{-3}$ and $2 \cdot 10^{-2}$) C mm⁻².

Figure 2: Carbon (C-KLL), oxygen (O-KLL) and copper (Cu-L₃M₄₅M₄₅) Auger peak intensity on chemically cleaned copper as a function of electron dose.

Figure 3: C-KLL peak shift to higher kinetic energy with increasing electron dose. The arrows show the shift of the peak maximum to higher kinetic energy with increasing electron dose.

Figure 4: Direct N(E) Auger electron spectra of an air exposed niobium thin film acquired after an electron exposure of ($2 \cdot 10^{-6}$, $4 \cdot 10^{-5}$, $4 \cdot 10^{-4}$ and $4 \cdot 10^{-3}$) C mm^{-2} .

Figure 5: Carbon (C-KLL), oxygen (O-KLL) and niobium (Nb-M₄₅N₂₃V) Auger peak intensity as a function of electron dose. The sample is an air exposed niobium thin film.

Figure 6: The SEY at 2.5 keV PE energy as a function of electron dose. SEY values are calculated with Equation (1), using the sample drain current measured with biases of +18 V and -18V.