ROLE OF SURFACE CHEMISTRY IN CONDITIONING OF MATERIALS IN PARTICLE ACCELERATORS

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Abstract

For the vacuum scientists and the accelerator community, finding solutions to mitigate pressure rises induced by electron, photon and ion desorption, and also beam instabilities induced by ion and electron clouds is a major issue. Along the time, changes in the surface chemistry of vacuum chambers are observed during beam operations, leading to modifications of: outgassing rates, stimulated desorption processes and secondary emission yields (SEY).

To understand the role of the surface chemistry of air exposed materials in the electron conditioning process, typical air exposed materials used in particle accelerators : thin film coatings (NEG, i.e a Ti-Zr-V alloy, and carbon), copper (and its oxides Cu_2O and CuO) and niobium were conditioned by low energy electron irradiation for a better understanding of electron-cloud effect. First, SEY was measured to understand the changes of surface conditioning upon particle irradiation; then, surface chemistry evolution after electron irradiation was investigated by both XPS orTOF-SIMS analyses using the ANDROMEDE facility at IJCLab. Finally, the relationship between the surface chemistry and the conditioning phenomenon will be discussed.

INTRODUCTION

Electron emission is a major phenomenon involved in the formation of the electron-cloud (EC) in the LHC. EC effects have been identified among the major performance limitations for the Large Hadron Collider (LHC). The EC is induced by the electron multipacting process related to the secondary electron yield (SEY) of the surfaces exposed to electron irradiation. The SEY depends strongly on the nature of materials and on the surface chemistry, and consequently the EC formation is determined by the surface properties. Nevertheless, electron bombardment of the inner surface of the beam pipes is also responsible for a beneficial effect called "surface conditioning" (or the "scrubbing effect") leading to a reduction of SEY and therefore inducing a mitigation of the multipacting process and electron cloud build up.

The aim of this study was first to validate the set-up developed in our laboratory and devoted to SEY measurements, by reproducing the results that exist elsewhere for Cu and Nb for instance. Then, we proposed an alternative method for the analysis of the surface chemistry to the X-ray Photoelectron Spectroscopy which is traditionally used: Time-of-Flight Secondary Ion Mass Spectrometry with high energy gold nanoparticles to probe the surface. We investigated the conditioning of copper beam screen induced by electron bombardment and identified the role

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played by the modifications of the surface chemistry in this phenomenon.

EXPERIMENTAL DESCRIPTION

The experimental set up for SEY measurements is an in-house build set-up developed at IJCLab. It consists of a single UHV chamber (base pressure: $7x10^{-10}$ mbar) equipped with an electron gun providing a pulsed electron beam (with a pulse length of 30 ms) in the energy range 10 to 4000 eV, with an intensity from few nanoamperes to 50 µA. The sample is carried by a single manipulator allowing for a precise positioning of the sample in the chamber.

The SEY was measured by the sample bias method that is a two-step SEY measurement. First, the primary current I_p is acquired for each primary electron energy E by applying a positive sample bias (V=+50 V). In this case, the current measured on the sample is $I_M(+50V) = I_P$. The emitted secondary electrons (SE) are trapped and recaptured by the sample. The sample polarity is then switched to a negative value (V=-20 V) and I_M is acquired while shooting with the electron gun on the sample with the same energy settings as during I_p acquisition. The SE current (I_{SE}) is given by:

$$I_{SE} = I_p - I_M(-20V) \tag{1}$$

The SEY δ is then obtained by:

$$\delta = \frac{I_{SE}}{I_p} = \frac{I_p - I_M(-20V)}{I_p} = 1 - \frac{I_M(-20V)}{I_M(+50V)} \tag{2}$$

In the present work, we used the ANDROMEDE facility [1] to analyse samples of copper beam screen. 12-MeV Au_{400}^{4+} ion beams are accelerated by a NEC Pelletron® 4MV electrostatic accelerator to bombard samples. The emitted secondary ions (both positive and negative ions) are analysed with the ToF spectrometer EVE In this set-up, it is possible to record a mass spectrum with only one single ion impact. Consequently, the secondary ion emission yield is strongly enhanced and the sensitivity of chemical surface analysis is improved. A high detection efficiency for molecules deposited in very small quantities on metal surfaces (lower than the monolayer) is reached. Moreover, the limited number of primary ions (about 107 nanoparticles/cm2) required to analysis the samples prevents excessive damage of the surface. Only the extreme surface (i.e. the molecules deposited on the surface and the materials surface corresponding to a depth of ≈10 nm) is analysed.

The experimental system used for XPS analysis in the present work is the K-ALPHA system from Thermo-Fisher, equipped with a monochromatic Al kα X-ray source (hν=1486.6 eV) and an Ar^+ ion gun for XPS sputter depth profiling. For each analysis, a full energy spectrum

is acquired for identification of the constituent elements and additional sweeps are then performed in narrower energy regions to obtain high energy-resolution spectra. Spectra displayed in the following in normalized intensity were obtained after normalization of the signal to its maximum intensity.

The following samples were analysed : an OFE-Cu, a Cu_2O sample provided by the NEYCO company, CuO produces via a chemical route on Cu [2], a Ti-V-Zr coating deposited on Cu (non-activated NEG) and a Nb sample (provided by the company Tokyo Denkai).

SECONDARY ELECTRON YIELD EVOLUTION

To illustrate the SEY evolution during electron-conditioning, results obtained for an as-received copper beam screen sample during its irradiation at room temperature by 500 eV electrons is shown in Figure 1. SEY is observed to decrease over the full considered energy range when the irradiation dose increases. The maximum SEY, initially equal to 2.00, decreases down to 1.10 after a dose of $6 \cdot 10^{-2}$ C/mm^2. For larger irradiation doses, no further evolution of SEY is observed. These results are in good agreement with those previously published in the literature: the initial value of the SEY for an as-received copper is reported to be between 2.5 and 2.0 and for a conditioned sample the SEY decreases down to a value between 1.2 and 1.1 [3-5].

Typical conditioning curves, i.e. evolution of the maximum SEY with respect to electron irradiation dose, of air exposed samples (namely Cu, CuO, Cu_2O, Nb, NEG coating and Carbon-coating) are given in Figure 2. It is seen that the maximum SEY of metallic sample (Cu and NEG) decreases from an initial value around 2.1 down to an ultimate SEY (maximum SEY at the saturation of the decrease) of about 1.1. The saturation of the SEY decrease is obtained for doses higher than 10^{-3} - 10^{-2} C/mm^2. As shown in other studies, the SEY of the conditioned carbon deposit is well below one. This is why it can be used as an antimultipacting layer in accelerator beamlines. A surprising result was obtained for CuO, since its SEY in a fully conditioned state is also less than one: it reaches a SEY value close to 0.8 after electron-conditioning. This result is in agreement with a study that shows a SEY for a CuO nanolayer lower than one [6]. However, it was recently mentioned that CuO should not condition easily [5]. This discrepancy could come from the influence of the thickness of the CuO layer, or from the effect of a possible difference in the stoichiometry of the CuO samples used in the different studies. The SEYs for the other materials are consistent with the literature.
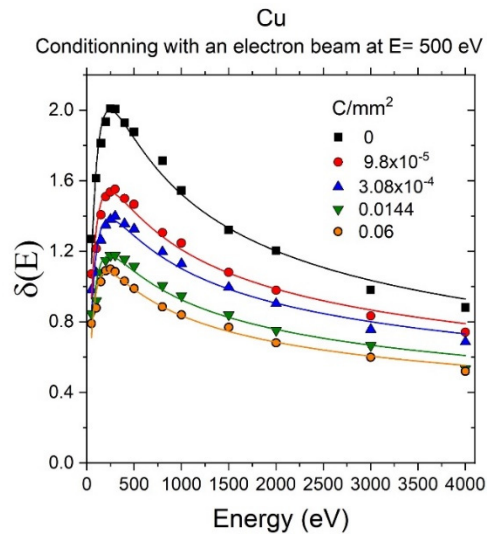

Figure 1: Secondary electron yield curves as a function of primary electron energy, for an as-received copper beam screen conditioned with a 500 eV electron beam at different irradiation doses.
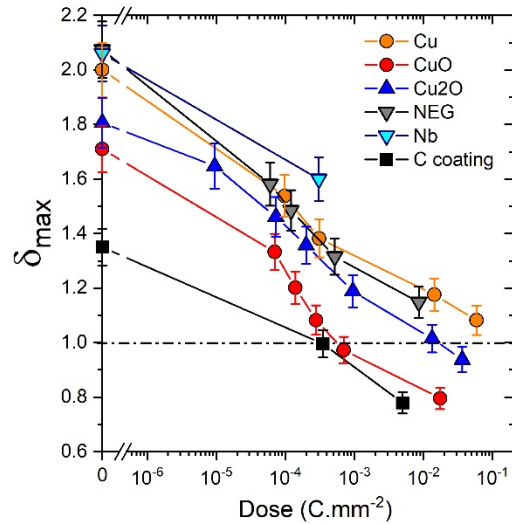

Figure 2: δ_{max} as a function of the dose for different impinging electron energies on several materials conditioned with a 500 eV electron beam: Cu, CuO, Cu_2O, Nb, NEG coating and Carbon-coating.

SURFACE CHEMISTRY EVOLUTION

Evolution of the Cu-surface after electron-conditioning was more particularly investigated. In the as-received state, the C 1s line shows a main peak at 284.8 eV ascribed to C-C bonds (sp3 hybridization). A second peak at 286 eV corresponding to C-O bonds, and a third at 288.2 eV related to O-C=O groups are visible (Figure 3). These latter are due to an adventitious carbon contamination and comes from the different compounds forming the adsorbed layer. In the fully conditioning state (Figure 3b), the XPS analysis indicates that the decrease of the secondary electron yield corresponds to significant modifications of the surface chemistry. The disappearing of the peak at 288.2 eV on the C 1s line implies the removal of O-C=O groups. The main

C 1s peak is shifted towards 284.8 eV, indicating the transformation of the adventitious carbon layer (sp3) into a more graphitic form (sp2), as already observed in previous studies, for instance in [4]. This phenomenon is called sometimes "graphitization". Figure 3c shows the XPS analysis of a carbon coating layer provided by the CERN: we found the main C 1s peak related to the sp2 hybridization.
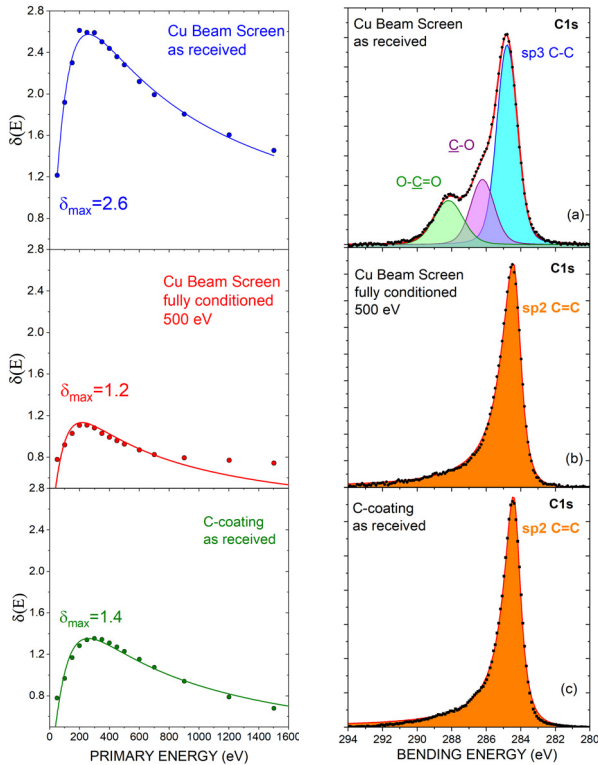

Figure 3: SEY curves and C1s XPS spectra measured on a LHC Cu beam screen sample: (a) "as received"; (b) fully conditioned; (c) on an as received amorphous carbon coating.

From the analysis of the negative secondary ion spectra recorded with ANDROMEDE, a significant increase of carbon (C_n^-) and carbon cluster (C_nH^-) emission for the conditioned Cu sample is observed (Fig. 4). Comparison of the conditioned sample spectrum with a graphene spectrum obtained under the same conditions suggests that a film of hydrogenated graphene covers the irradiated surface as the carbon cluster distribution is similar. Thus, in agreement with the XPS results, the ToF-SIMS analysis shows that a carbon layer whose bonds are that of graphene (sp2 hybridization) is formed on copper surface under electron bombardment. It is worth noting that this carbon layer is not composed only of carbon, but it contains also high amounts of hydrogen and oxygen.

Evolution of the CuO surface chemistry during electron-conditioning was also investigated by XPS. Figure 5 shows the XPS Cu 2p lines for an as-received and a fully conditioned CuO sample. The Cu 2p satellite shape on the as received sample spectrum is the signature of a CuO sample. After electron conditioning, the intensity of the Cu 2p satellite strongly decreases, indicating that the conditioned

area was partially transformed into Cu_2O. Thus, the electron irradiation produced a partial reduction of CuO into Cu_2O.
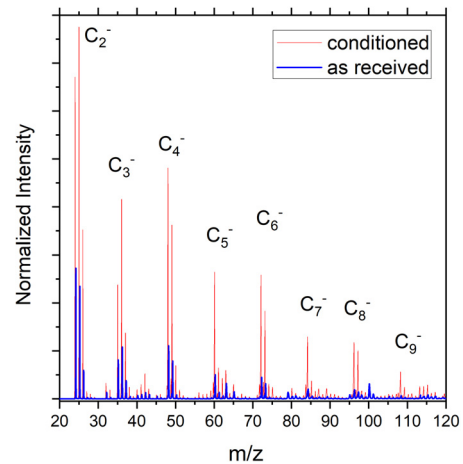

Figure 4: Negative secondary ion mass spectrum for a copper beam screen after electron conditioning process displaying intense carbon cluster peaks.
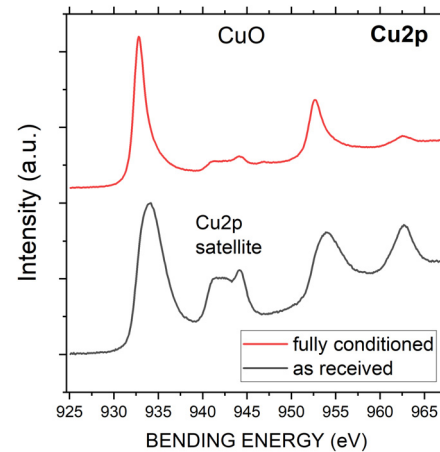

Figure 5: Cu2p XPS spectra measured on a CuO layer deposited on Cu.

CONCLUSION

Conditioning effect was investigated for several materials by measuring the variation of their SEY with the electron dose. Study of the copper beam screen conditioning under irradiation with 500 eV electrons evidenced two processes: (i) a surface cleaning by electron stimulated desorption; (ii) the formation of a graphene-like layer. Both processes lead to the decrease of the copper SEY down to value close to unity. Carbon transformation upon electron irradiation should be also an effective phenomena to explain the SEY decrease with the electron dose for the other metallic materials, for which the SEY of a fully conditioned state is close to one. A SEY value below 1 after conditioning for CuO represents also an interesting result since it is close to the SEY of carbon-coating, this latter being known for its antimultipacting properties. Further investigations are needed to explain the conditioning of CuO.

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