

NEAR-SURFACE COMPOSITION OF ELECTROPOLISHED NIOBIUM BY VARIABLE PHOTON ENERGY XPS

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Abstract

The mechanical and other damage to the interior surfaces of niobium cavities for superconducting radio-frequency accelerators is removed by either buffered chemical polish or by electropolish. The effect of each on SRF performance has been extensively reported, with much attention given to the near-surface composition. In particular, angle-resolved XPS has been used to elucidate the sequence of oxides. We report first results of an alternative approach, varying the x-ray photon energy at normal incidence to accordingly obtain information from different depths. The experiments were performed on Beamline X1B at National Synchrotron Light Source.

BACKGROUND

The mechanical and other damage to the interior surfaces of niobium cavities for superconducting radio-frequency accelerators is removed by either buffered chemical polish or by electropolish. The effect of each on SRF performance has been extensively reported, with much attention given to the near-surface composition [1]. The earliest XPS work [2,3] already envisioned a layer sequence of Nb metal – Nb suboxide(s) – Nb₂O₅. Since then, many workers have used angle-resolved XPS, seeking to elucidate the sequence of oxides [4 - 7]. The underlying principles are that 1.) the travel length in the solid of photoelectrons belonging to a specific peak is fixed, so that collecting only those exiting at a shallow angle to the surface accordingly makes the information depth shallow. As a practical matter, about a factor of 2 is attainable, though the angular aperture of the electron spectrometer at successively shallower take-off angles must also be considered. 2.) The binding energies of Nb in the various oxides are sufficiently different compared to the energy resolution and signal/noise of the XPS machine that their contributions can be separated and quantified. 3.) The Nb surface examined can be represented as a stack of uniform planes of the successive oxides, each being identical to its pure bulk, on a slab of Nb metal. Finally, surface roughness on the scale of the inelastic mean free path (IMFP) a few nm and grain boundaries within the analyzed area (a few mm) can be a source of complications.

PRESENT STUDY

We report initial results of an alternative approach, varying the x-ray photon energy at normal incidence, thus correspondingly varying the photoelectron kinetic energy

and IMFP accordingly to obtain information from different depths. A first advantage is that IMFP can be varied over a wider range than attainable by changing angle. Nb's IMFP is calculated to range from 0.75 nm to 3.22 nm as electron kinetic energy varies from 200 eV to 1600 eV [8]. Square-root extrapolation to 100 eV is probably reasonable [9], indicating a value near 0.5 nm as the minimum, a factor of more than 6 in total. For photoelectrons originating from the Nb 3d 5/2 level (202.2 eV), the corresponding photon energies range from about 300 eV to 1800 eV. A second advantage is that geometry does not change as IMFP is varied; any contribution of roughness remains constant, as does variation of IMFP across the collection lens angular aperture. The application of variable photon energy photoelectron spectroscopy to investigate the oxide/metal interface of a Nb single crystal has been reported [10].

The material examined was a 15 mm diameter disc cut from high-purity Nb sheet used for SRF cavity production at Jefferson Lab, having a vendor-supplied RRR =592. The cut disc was first subjected to 1:1:1 (volume) mixture of phosphoric, nitric and hydrofluoric acids, referred to as BCP, at < 10°C for 50 minutes, which is expected to remove nominally 400 µm of material. After rinsing, it was annealed for 24 hours at 1200 °C at a pressure below 10⁻⁸ torr, yielding a grain size of a few millimeters. The disc was then electropolished “EP” in a 90/10 (volume) solution of sulfuric acid and hydrofluoric acid at 30°C and a current density of 50 mA/cm² for time sufficient to remove nominally 50 µm from the surface. We examined the surface topography by atomic force microscopy (AFM) using a Digital Instruments Nanoscope IV in intermittent contact mode (“tapping mode”). A series of 20 micron square fields gave an RMS roughness of 25 nm. We also examined three 3 mm fields using stylus profilometry (“Dektak”) and found an RMS roughness of 0.78 microns.

The photoelectron spectroscopy experiments were undertaken on soft x-ray undulator beamline X1B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This beamline is equipped with a spherical grating monochromator and focusing mirrors to attain a minimum spot size of 100 µm x 30 µm. After rinsing with reagent-grade isopropanol, the sample was introduced to the vacuum chamber and pumped to a base pressure below 10⁻¹⁰ torr. Spectra spanning the Nb 3d manifold were collected at photon energies of 352 eV, 520 eV and 1000 eV, corresponding

to IMFP's of 0.68 nm, 1.0 nm and 1.9 nm in Nb metal [8]. Fig.1 shows the as-acquired data.

In order to extract the different components in the Nb 3d spectra, a curve fitting procedure was applied. A Doniac-Sunjic line shape was assumed where a Lorentzian width of 180 meV was used for all components [11]. The spin split was set to 2.74 eV and the branching ratio was kept at 2/3. The shifts for the oxidation states were kept close to those of [7]. The background was modeled by adding a Shirley background to an exponential. The Gaussian width of the peaks was found at each photon energy by letting the fitting routine find the width of the prominent Nb 5+ component while the others were kept fixed. The other widths of the other components were then set to this value and all were allowed to vary, but converged to about the original value. In each case, the experimental data were first fit with metal, 5+ and 4+, adding other contributions as needed. Figs. 2–4 show the fits with the minimum set in each case and the residual.

While much more data is needed to reach conclusions about the variation niobium species with depth below the surface, the present results make clear that photoelectron spectroscopy with variable photon energy is an important tool.

ACKNOWLEDGEMENTS

The Boston University program is supported in part by the Department of Energy under DE-FG02-98ER45680. The X1B endstation is funded by the U.S. Army Research Office under Grant No. DAAD19-01-1-0364. The NSLS is supported by the U.S. Department of Energy, Division of Materials and Chemical Sciences. The Jefferson Lab work is supported by the U.S. Department of Energy under DE-AC05-84ER40150.

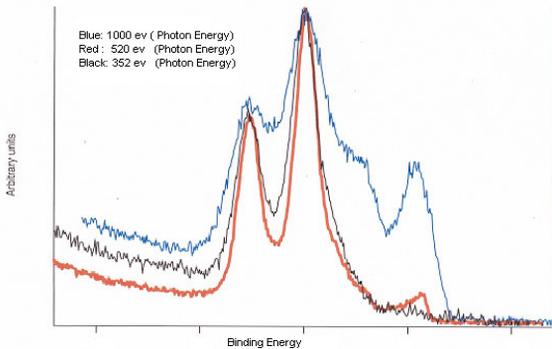


Figure 1: Raw data.

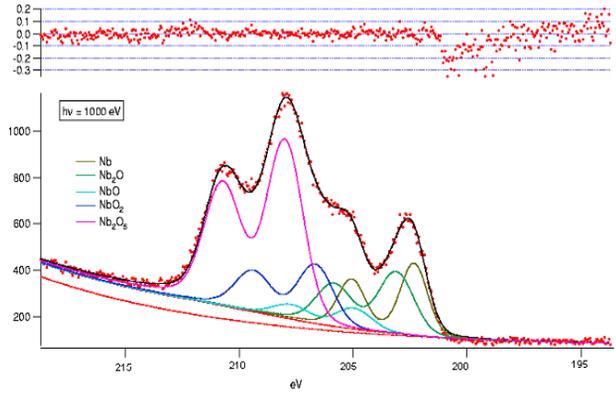


Figure 2: X-ray energy = 1000 eV.

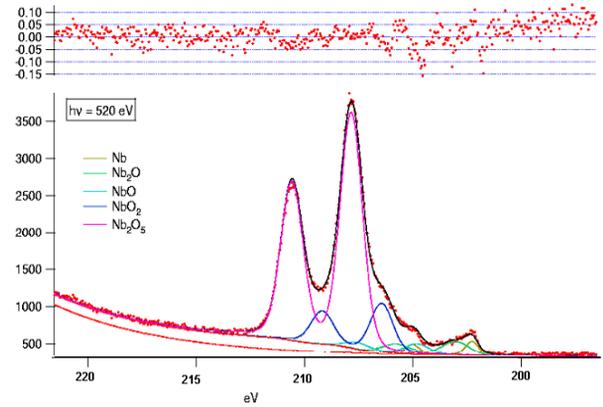


Figure 3: X-ray energy = 520 eV.

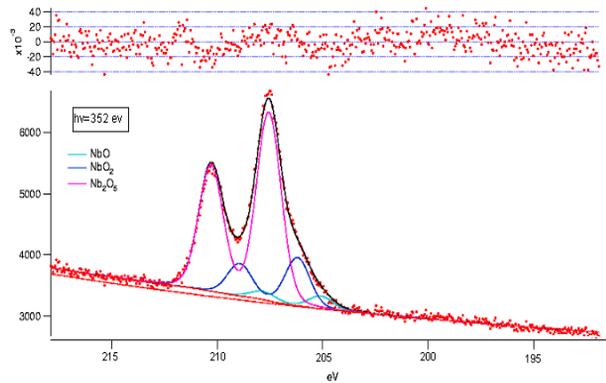


Figure 4: X-ray energy = 352 eV.

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