XPS STUDIES OF NITROGEN DOPING Nb SAMPLES BEFORE AND AFTER GCIB ETCHING*

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Abstract

The surface chemical composition of nitrogen doping Nb samples used for the fabrication of superconducting radio frequency (SRF) cavities, followed by the subsequent successive EP with different amounts of material removal, has been studied by XPS. The chemical composition of Nb, O, C and N was presented before and after Gas Cluster Ion Beams (GCIB) etching. No signals of bad superconducting nitrides NbN_x was found in any doped and un-doped samples before etching. However, in the depth range greater than 30nm, the content of N elements is below the XPS detection precision scope even in the samples directly after nitrogen doping treatment.

INTRODUCTION

Niobium used for cavity production undergoes several different treatments before it eventually becomes a superconducting radio frequency (SRF) cavity ready for test. The typical procedures not only includes rolling, deep drawing, electron beam welding and other mechanical treatments, but also includes chemical etching, high temperature degasing, high pressure rinsing, 120^0C baking and other post treatments. The subtle material details of the niobium surface largely influence the surface resistance of niobium below 2K. XPS analysis of the surface composition of niobium used for the fabrication of SRF cavity after procedures commonly employed in the preparation of SRF cavities have been reported [1-2]. Nitrogen doping is a new surface treatment discovered by A. Grassellino [3], which can systematically improve the quality factor of SRF niobium cavities up to a factor of about 3 compared to the standard surface treatment procedures. Presently, nitrogen doping treatment is being transferred from the prototyping and R&D stage to the production stage [4]. Fundamental understanding of the nitrogen doping mechanism is being carried out extensively, but yet remains unclear. The SRF cavity directly after nitrogen doping treatment showed quality factor in the range of 10^7 at 2K. That is far below the routinely achieved Q values of cavities with the standard surface treatment procedures at this frequency and temperature. This has always been thought to be caused by the formation of unwanted poorly superconducting nitrides [3]. Thus the aim of the present study is to investigate the elemental compositions and chemical structures of the niobium samples with different treatments. The X-ray Photoelectron Spectroscopy is suitable to provide this information. For this reason XPS studies of nitrogen doping samples before and after gas cluster ion beam (GCIB) etching has been carried out, with particular attention to the elemental compositions and chemical structures of nitrogen both on the surface and in the penetration depth range.

EXPERIMENTAL

To avoid heat generation, instead of wire electro-discharge machining (EDM), the niobium samples were manually processed. The niobium strips were polished smoothly on 180-grit sandpaper, 300-grit sandpaper and 1200-grit sandpaper. The samples' treatments were attempted to replicate that of the cavities. So the niobium strips were etched by EP (HF:H_2SO_4=1:9), with the material removal of about 150μm, to remove the mechanical damage layers and surface contaminations introduced during handling or exposing to the air.

Nitrogen Doping Treatment

The nitrogen doping treatments and 800^0C heat treatments of the niobium samples used for the magnetic measurements can be seen in [5].

XPS Measurements Before Etching

The elemental compositions and chemical structures of the niobium samples was analysed by using a Thermo Scientific ESCALab250Xi Multifunctional Photoelectron Spectrometer. Photoelectrons are excited by using a monochromatized source that produces Al Kα (hv=1486.6eV) radiation and the power is about 200W. The surface area of analysis of the sample is about 500μm×500μm. A base pressure of about $3×10^{-10}$mbar is obtained in the analysis chamber. Both doped and un-doped samples from two groups were chosen for the XPS experiments. That is ND-1st-0μm, ND-2nd-0μm, ND-2nd-1μm, ND-2nd-7μm, ND-2nd-13μm, ND-2nd-21μm, HT-2nd-0μm 、 HT-2nd-20μm and noNDnoHT. The labels begin with ND, followed by a serial number and ended by a exact number means a doped sample from group 1 or group 2 with a certain amount of EP removal.

A lower resolution survey over the wide energy window with the bin size of 1 eV is used to get information about elements presentation the sample. High resolution scans around peaks corresponding to the elements of interest are then performed with the bin size of 0.05 eV to obtain the fine structure of the peaks, which contain the information about the chemical environment.

XPS Measurements After Etching

To obtain the elemental compositions and chemical structures in the penetration depth, XPS studies were

carried out on both the doped and un-doped niobium samples after different amounts of GCIB etching, taking its advantage of reducing the damage introduced to the specimen during depth-profiling. Argon is used in GCIB treatments because of its chemically inert and inexpensive. Argon clusters bound together with Van der Waals forces have average cluster size of about 500 atoms; the average

cluster charge is +1. Three etchings were performed on each sample surface; the average cluster energy is 5keV, 10keV, 15keV, respectively. For each time, the etching time is 30 minutes. The corresponding etching depth of 5keV for 30 minutes is about 30nm. After each time of etching, a lower resolution survey and high resolution scans were performed on the new surface.
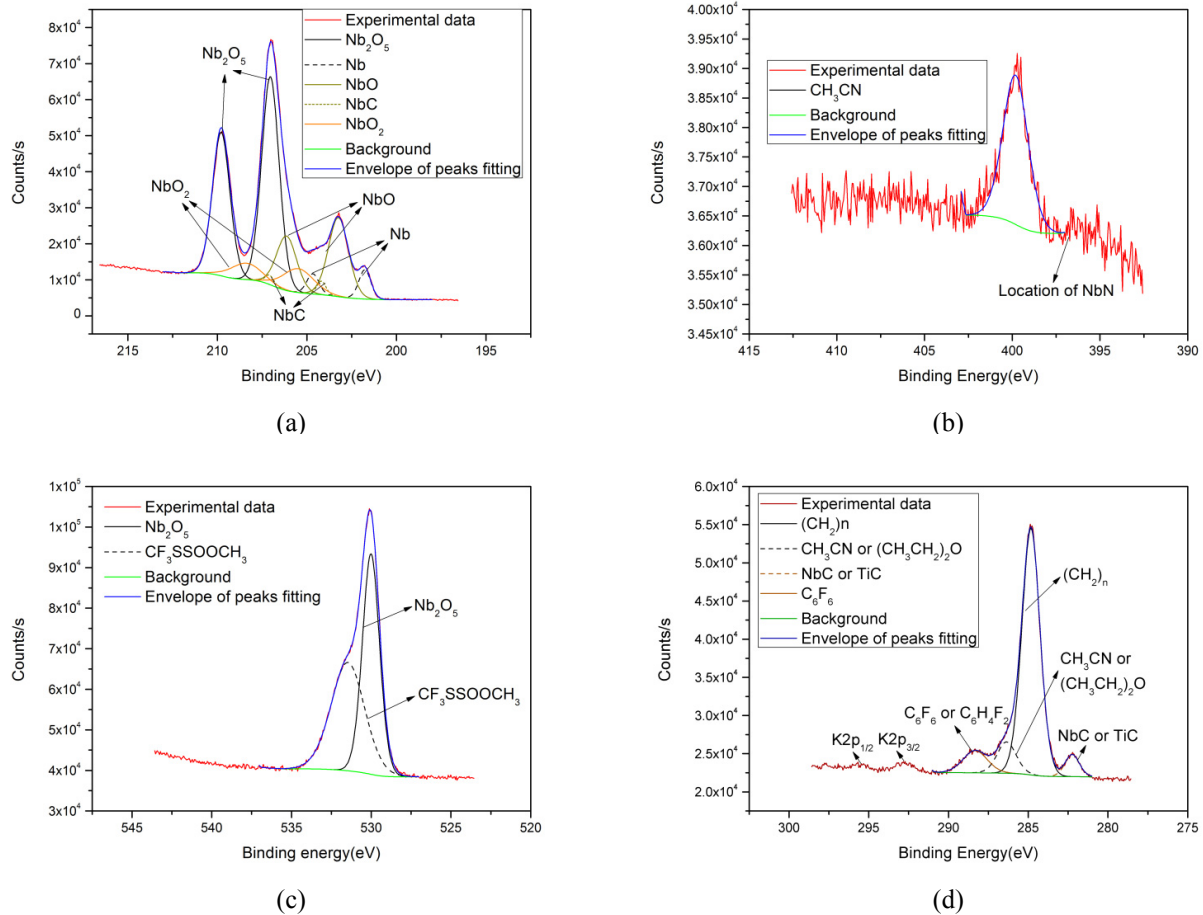

Figure 1: XPS spectra of Nb 3d (a), N 1s (b), O 1s (c) and C 1s (d) of the ND-2nd-0μm sample.

RESULTS

On the Surface

After the analysis of XPS results, the elemental compositions and chemical structures on the surface of niobium samples with different treatments were obtained. The XPS spectra of Nb 3d and N 1s of the ND-2nd-0μm sample are shown in Figs 1. Niobium in the surface layer formed after nitrogen doping treatment without subsequent EP material removal occurred in Nb_2O_5, NbO, NbO_2 and NbC. The signal peak of nitrogen has good symmetry, which means the chemical distribution of N is relatively simple. Compared with the standard energy spectrum, nitrogen in the surface layer of sample directly after nitrogen doping treatment may possibly occurred as CH_3CN for the binding energy of 399.84eV. No nitride was detected in the surface layer of the sample directly after nitrogen doping treatment. Oxygen in the surface

layer of sample directly after nitrogen doping treatment occurred as Nb_2O_5 and compound formed together with other elements in the surface layer. Carbon .in the surface layer of sample directly after nitrogen doping treatment mainly occurred as hydrocarbon which can be considered contamination.

The elemental compositions and chemical structures on the surface of all niobium samples with different treatments were basically the same. No nitrides were found on all the surfaces of the samples. That means the poor quality factor of nitrogen doping SRF cavities without subsequent EP material removal is not due to the formation of bad superconducting nitrides.

In the Penetration Depth

For C elements, after GCIB etching, within the depth below 30nm from the surface layer, the interior of the sample is substantially free of hydrocarbons and C mainly exists in the form of NbC or TiC. For O elements, the

Fundamental SRF R&D

Bulk Niobium

main distribution forms are Nb_2O_5 both before and after GCIB etching. However, in the depth range below the surface layer of 30nm, due to the reduction or absence of C, F, S, the other compositions of O is not detected. The GCIB etching depth exceeds the depth of the niobium oxide distribution, so niobium mainly occurs as Nb after etching. But the amount of nitrogen diffused into niobium is minimal. So after the GCIB etching depth of 30nm, no effective signal peaks for N were detected during the 5 minutes collection time, as can be seen in Figure2.
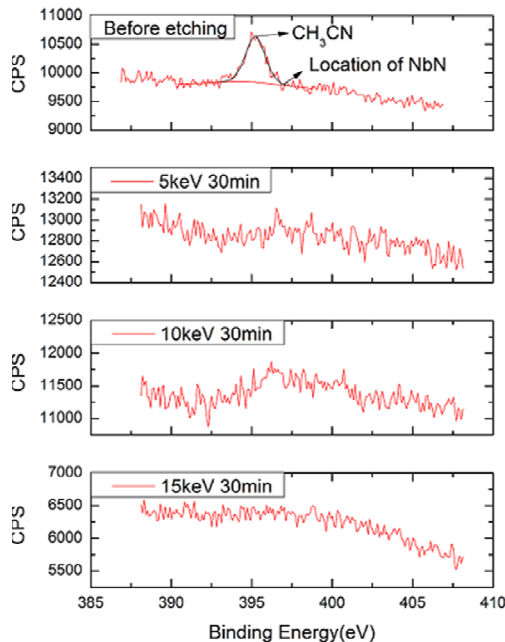

Figure 2: XPS spectra of N 1s of the ND-2nd-0μm sample before and after GCIB etching.

XPS test results of other samples after GCIB etching are similar to that of the ND-2nd-0μm sample,

CONCLUSION

The elemental compositions and chemical structures both on the surface and in the penetration depth range of niobium samples with different treatments have been carried out by using XPS. No signals of bad superconducting nitrides NbN_x was found in any doped and undoped samples before GCIB etching, which means that the poor quality factor of nitrogen doping SRF cavities without subsequent EP material removal is not due to the formation of bad superconducting nitrides. Combined with the magnetic property measurements of nitrogen doping niobium samples [6], the high concentration of nitrogen impurity at the surface layer of the SRF cavity directly after nitrogen doping treatment is a possible cause of the cavity's extremely low quality factor.

After GCIB etching, within the depth below 30nm from the surface layer, the content of N is lower than the XPS detection accuracy. It means that the doped nitrogen is trace and special attention is needed to the control of the nitrogen doping conditions.

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