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ELECTRON-ACTIVATED CARBON DIFFUSION IN NIOBIUM COMPOUNDS FOR RF SUPERCONDUCTIVITY*

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ABSTRACT

The higher energies planned for the next generation of particle accelerators and storage rings makes the use of superconducting hi-Q RF cavities highly desirable. Past efforts to produce reliable cavities for such projects have met with limited success. Among the barriers to achieving the maximum electric field gradient are oxide layer charging, single surface multipactoring and field emission. These are surface effects.

At SLAC, a multi-technique (AES, XPS, ellipsometry, EID, etc.) surface analysis system has been constructed to examine possible sources of these problems and to suggest processes or surface coatings which will reduce or eliminate them.

As one component of this analysis, we have investigated the time evolution of species on anodized Nb_2O_5-on-Nb surfaces as a function of electron bombardment. The surface concentration of C increases at an anomalously high

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rate under the exciting electron beam. Examination of the surface and gas phase indicate that the C source is in the underlying material.

Estimates of the penetration depth of the beam are in agreement with the fact that there is a significant rate increase in the surface C buildup when the beam penetrates the anodized layer into the Nb bulk. Bulk analytical methods indicate, however, that the C concentration in the Nb is very low.

Grain boundary diffusion of C to the surface and/or an enhancement of the C diffusion coefficient due to localized beam pipe heating are examined as possible explanations of this effect.

INTRODUCTION

RF superconductivity applied to the operation of hi-Q RF cavities for u in various high energy particle accelerating machines has been a goal for some time. It is generally recognized now that surface effects are prominent among problems precluding the attainment of maximum electric field gradients. At SLAC we have initiated a general surface instrumental study of these surfaces, with the purpose of characterizing the causes of various problems (oxide layer charging, field emission, etc.) plaguing the cavities. We have investigated oxide layer charging by measurements of secondary electron emission coefficients, sputtering rates, chemical shifts and electron bombardment effects on anodized Nb_2O_5 layers on Nb.

During these measurements, electron-induced diffusion of C to the Nb_2O_5 surface from the underlying interface has been observed. Preliminary measurements of this effect are presented along with possible mechanisms for the observed surface C buildup.

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EXPERIMENT

The entire surface analytical system is described in some detail elsewhere[1]. Those portions relevant to the C data will be described here.

The vacuum system is of standard UHV design incorporating a CMA with axial electron gun for Auger electron spectroscopy (AES). An Ar ion gun was employed for depth profiling and thinning of anodized layers. The electron and ion gun axes were 30° and 41° to the surface normal, respectively. All measurements presented here used an electron beam of 2 keV energy, 10μA current, .021 cm diameter and 29 mA-cm^{-2} current density. The Ar^+ beam was 1 keV, unscanned with a beam diameter of 5mm FWHM and 62μA-cm^{-2} current density.

The solid Nb substrates were prepared from low-Ta, low-C (30ppm measured prior to outgassing) e-beam melted material. Discs were cut and machined to 0.1cm thickness from previously outgassed (2500 K) rods. The resulting surfaces had large grains 1 cm in diameter and were essentially single crystals as thick as the sample disc.

The Nb surfaces were degreased and electropolished in 10% HF-90% H_2SO_4 solution to remove approximately 50 μm of surface. Samples were then anodized to various thicknesses in 3% NH_4Cl solution using a pure Nb cathode. A value of 24 Å/V was used to calculate the oxide thickness. The anodizing voltage was removed when the current fell to 1% of its initial value.

MEASUREMENTS

From work by others[2] and measurements by us[1], we have determined that two of the AES Nb transitions are characteristic of the Nb metal and oxide surfaces. These are the 165 eV (designated Nb (ox) here) and 170 eV (Nb (met))

lines of Nb. The AES sensitivities for these lines, for O and for C have been determined using clean and anodized Nb and graphite and are used to properly scale the AES data presented.

The results for a representative sample (Figure 1) are presented in Figures 1 a, b, and c. The data was taken as follows. A Nb substrate with an 1100Å anodized layer was inserted into vacuum and pumped down without bakeout until the pressure effectively stabilized at approximately 1×10^{-9} torr. The d.c. electron beam bombarded the surface while the AES peak heights were monitored as a function of time (Figure 1a). The sample was then sputter thinned to 593Å, at which time the electron beam was again turned on and the peaks monitored (Figure 1b). This process was repeated at 164Å (Figure 1c).

RESULTS

The 1100Å layer, as inserted, is stoichiometric Nb_2O_5 (checked by X-ray) with a superficial C layer which disappears after a short sputter etch. Data taken on graphite and powdered NbC samples show that the AES C peak observed in Figure 1 is typical of graphitic (or possibly amorphous) C. This observation of C peak shape is consistent with other work[3,4] on C.

When the electron beam bombards the surface (Figure 1a), the pentoxide surface is decomposed and some Nb (met) is produced[2]. Concurrent with this is a rise in the C signal, the source of which is probably C-containing molecules (CO, mainly) from the gas phase. Assuming a worst case sticking probability of one, the gas phase concentration of such molecules is just sufficient to account for this slow C signal rise. It is also possible that the C source is elsewhere on the surface or in the pentoxide layer. Its source in the layer is not likely (see Figure 1b and 1c at $t - 0$).

Comparison of Figures 1 a-c lead us to believe that the C is bound on top of any metallic Nb present in preference to binding to a Nb (ox) specie. In fact, as the C layer begins to increase in Figure 1a, the Nb (met) signal increase due to electron dissociation of the pentoxide is balanced and finally exceeded by the rate of C coverage, and the Nb (met) signal decays. When the Nb (met) atoms available as sites are saturated by C, the C spreads to Nb (ox) sites and the Nb (ox) signal then decays. The dissociated O is pumped away as O_2 or diffuses out of the layer to which AES is sensitive.

After the surface has been sputter thinned to 593A (Figure 1b), a very different behavior is observed under electron bombardment. The surface has been damaged by ion bombardment and all types of Nb oxides are present as well as O and Nb (met). The presence of O is inferred because the O/Nb ratio is greater than 2.5. When the electron beam strikes, chemical rearrangement starts to take place. Again the O signal decreases and, as C builds up, the Nb (met) signal rapidly drops off. The rate of C buildup is, however, considerably faster than can be explained by a gas phase source alone or from a surface diffusion source (there is no evidence of C in the sputtered area adjacent to the electron bombarded area, nor is there an appreciable increase in C during a one hour turnoff period of the electron beam).

The Nb (ox) signal rises rapidly initially and then levels off. Our AES sensitivity measurements on powdered Nb_2O_5, NbO_2 and NbO samples show that the Auger sensitivity for NbO_2 is considerably lower than that for the other two oxides. Thus, the initial rise in the Nb (ox) signal likely reflects an increase in AES sensitivity as NbO is formed from NbO_2, although proof awaits further investigation. Subsequent leveling off of Nb (ox) is due to: 1) a decrease in available Nb (met) sites for C bonding and so C spreads to Nb (ox) sites, and 2) an

equilibrium level being reached in the oxide rearrangement process.

After sputter thinning to 164Å (Figure 1c), behavior similar to that observed in Figure 1b is seen except that the experiment was extended for a longer period. The C rate increases in a manner suggesting a diffusion source of C feeding the surface. At these higher C coverages, even the surface O is being covered so that there is an increasingly rapid drop off in both the O and Nb (ox) signals once the Nb (met) sites are saturated.

DISCUSSION

In searching for the source of the C layer, we have eliminated gas phase and surface sources, as previously indicated. Considering the cleanliness of the Nb_2O_5 layer, we judge the remaining source possibilities to be the Nb bulk or Nb_2O_5-Nb interface. Measurement of the bulk C concentration in the Nb material used in this experiment indicates that some tens of microns of bulk C impurity atoms would be needed to produce the C coverages observed on the pentoxide surface. Figure 2 is typical of many depth profiles we have taken on various Nb substrates, anodized to different thicknesses from 100 to 1100 Å. All these measurements showed between a 10 and 20% concentration of C at the interface and a lower level of C into the Nb bulk. This agrees with AES depth profiles on unanodized Nb samples. These pure Nb samples show significant C and O contamination (from the atmosphere prior to insertion) which is removed by long sputtering times (equivalent to several hundred Å removed). Presumably, the activity of the freshly sputtered surface allows easy recontamination from the local gas phase or ion knock on. Once the surface has been cleaned though, it shows very little evidence of C and O. Figure 2 then would seem to show that

the C at the interface was there prior to anodization, and that this layer is spread for some distance into the Nb bulk during the depth profile.

We now turn to the mechanism by which the C may rapidly diffuse from the interface to the surface. Thermal diffusion by beam heating may be eliminated; calculations based on a variety of models[5,6] yield a maximum temperature rise of ~ 10K for electron beam heating for this experiment. We do note that the presence of the beam is necessary for the diffusion effect to occur. The electron penetration depth for 2 keV is ~ 650 Å [7]. We see that the C diffusion rate increased in the 164 Å and 593 Å layers but not the 1100 Å layer, so the beam apparently must reach the interface for such a rate increase to occur. The pentoxide layer may contain many grain boundaries and defects but these are not sufficient by themselves to account for the increased diffusion rates seen, although their presence may be necessary for the effect to occur. The most likely explanations, then, seem to be field or defect-enhanced rates and we are now exploring these with further experiments. Electron-activated enhancement of diffusion rates has been observed before[8]. If the effect is present in RF cavities, then C segregation under electron bombardment may be responsible for some of the effects noted in actual cavity structures. Reduction of multipactoring in cavities by careful increases in the electron loading fields may be due to a C layer forming on the cavity surface, resulting in a reduction in the secondary electron emission coefficient.

REFERENCES

1. E. L. Garwin, R. E. Kirby, T. Momose and E. W. Hoyt, 3rd European Conf. on Surface Science, Cannes, France, 1980.
2. T. T. Lin and D. Lichtman, J. Mater. Sci., 14, 1979, 455.
3. T. W. Haas, J. T. Grant and G. J. Dooley, J. Appl. Phys., 43, 1972, 1853.
4. M. A. Smith and L. L. Levenson, Phys. Rev., B16, 1977, 1365.
5. K. Roll, W. Losch and C. Achete, J. Appl. Phys., 50, 1979, 4422.
6. A. B. El Kareh, K. Y. Moravan and M. A. Smither, J. Appl. Phys., 48, 1977, 2356.
7. H. Kanter, Phys. Rev., 121, 1961, 461.
8. E. L. Garwin, E. W. Hoyt, M. Rabinowitz and J. Jurow, 4th Int. Vacuum Congress, 1968.

FIGURE CAPTIONS

1. AES signal vs. electron beam exposure time: a)1100Å, unsputtered, b) sputtered to 593Å and c) sputtered to 196Å.

2. Depth profile of 700Å anodic Nb_2O_5 layer on Nb. Sputter rate for Nb_2O_5 used throughout.

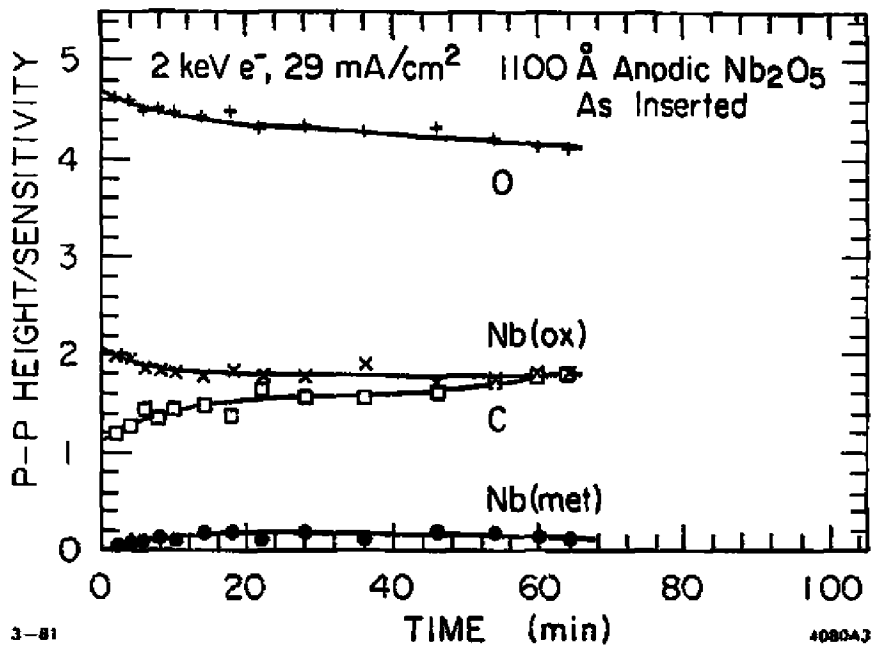
2 keV e⁻, 29 mA/cm²
1100 Å Anodic Nb2O5
As Inserted
O
Nb(ox)
C
Nb(met)
P-P HEIGHT/SENSITIVITY
TIME (min)
0
20
40
60
80
100
1
2
3
4
5
3-81
4080A3

Fig 1a

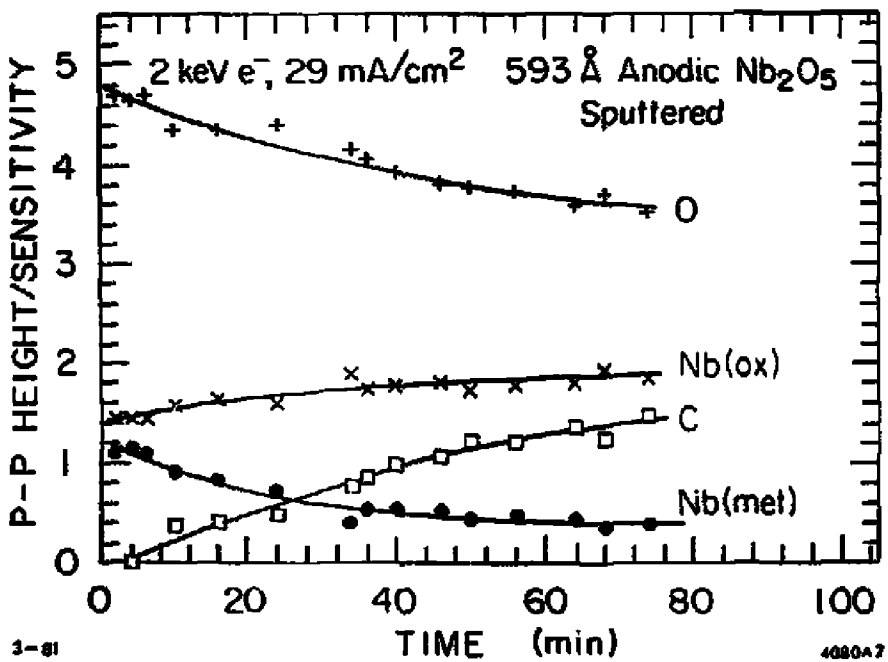
2 keV e⁻, 29 mA/cm² 593 Å Anodic Nb2O5
Sputtered
O
Nb(ox)
C
Nb(met)
P-P HEIGHT/SENSITIVITY
TIME (min)
0
1
2
3
4
5
0
20
40
60
80
100
3-81
4080A7

Fig. 1b

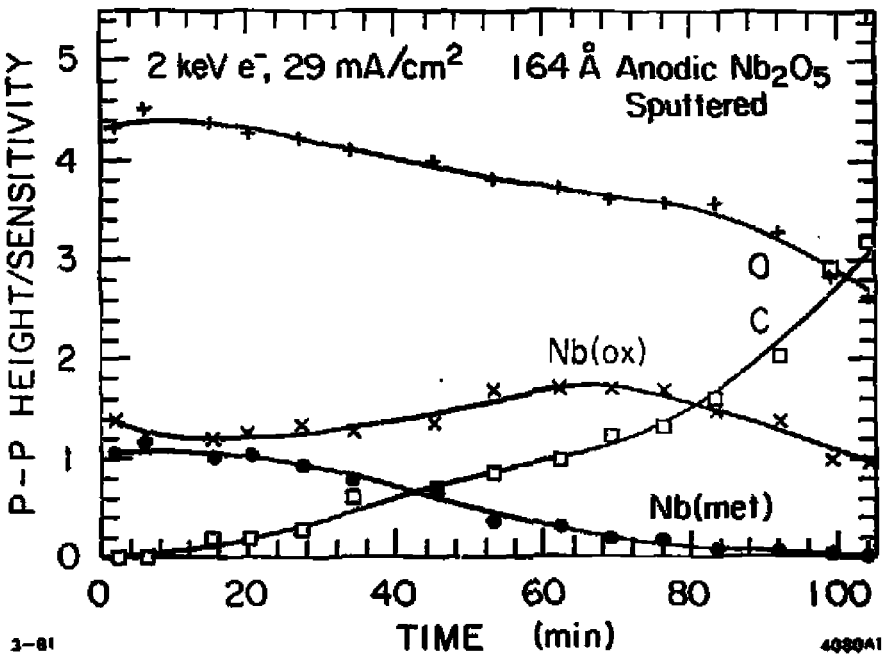
2 keV e⁻, 29 mA/cm²
164 Å Anodic Nb2O5
Sputtered
O
C
Nb(ox)
Nb(met)
P-P HEIGHT/SENSITIVITY
TIME (min)
0
1
2
3
4
5
0
20
40
60
80
100
3-81
4080A1

Fig. 1c

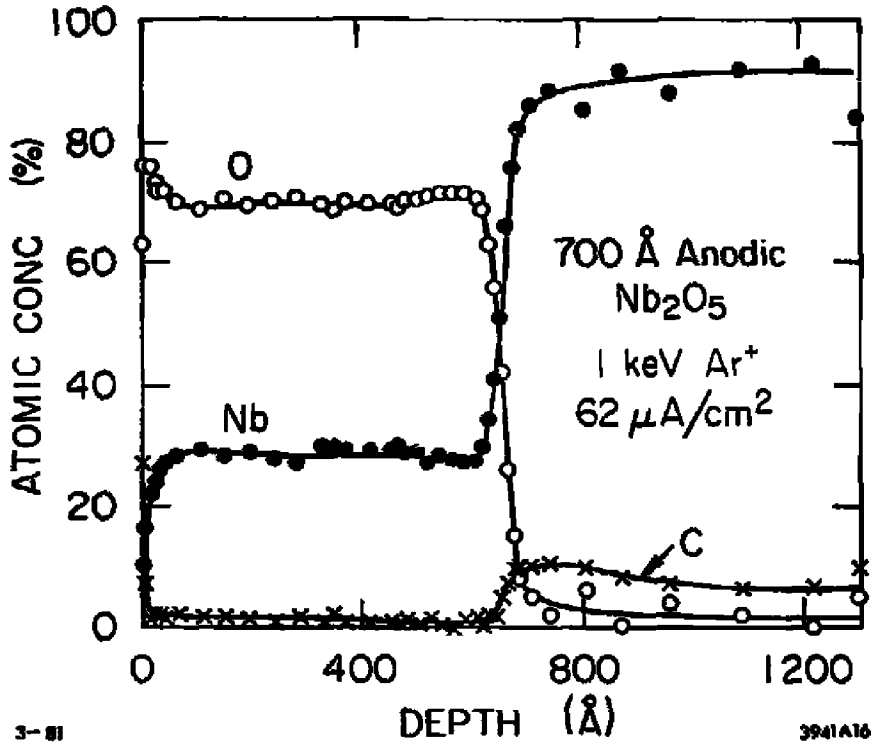
100
80
60
40
20
0
ATOMIC CONC (%)
O
Nb
C
700 Å Anodic
Nb_2O_5
1 keV Ar^+
62 $\mu A/cm^2$
0
400
800
1200
DEPTH (Å)
3-81
3941A16

Fig. 2