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**Surface Properties of Metal-Nitride and Metal-Carbide Films
Deposited on Nb for RF Superconductivity***

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ABSTRACT

Various effects occur which can prevent attainment of the high Q 's and/or the high gradient fields necessary for the operation of rf superconducting cavities. One of these effects, multipactor, both causes the cavity to detune during filling due to resonant secondary electron emission at the cavity walls, and lowers the Q by dissipative processes. TiN deposited onto the high field regions of room temperature Al cavities has been used at SLAC to successfully reduce multipactor in the past. We have therefore studied TiN and its companion materials, NbN, NbC, and TiC, all on Nb substrates under several realistic conditions: 1) as deposited, 2) exposed to air, and 3) 1 KeV electron-bombarded. The studied films (up to 14nm thickness) were sputter deposited onto sputter-cleaned Nb substrates. Results indicate that the materials tested gave substantially the same results. The maximum secondary electron yields for as-deposited films was about 1.0-1.2. These yields rose to greater than 1.5 upon air-exposure and were reduced to nearly the pre-oxidized values after electron bombardment (about 3×10^{17} electrons-cm⁻² in the case of NbN and NbC). XPS analysis showed that the oxides (e.g. TiO₂ in the case of TiN films) formed during air exposure were only slightly reduced (converted to lower oxides) by the electron beam exposure. AES showed a slight reduction in the surface O concentration following beam exposure. These results suggest that the chemical nature of top surface layers is responsible for the substantial changes in secondary electron yield observed upon electron beam exposure and that AES does not reflect this change strongly because of the difficulty in extracting chemical (versus elemental) information from AES. The results indicate that any of these films would be poor choices if simply deposited and exposed to air, but, in fact, the in-situ electron bombardment which occurs in cavities serves to reduce the effective secondary electron yield and thereby causes a substantial reduction in multipacting.

1. Introduction

Electron loading in RF superconducting cavity structures constitutes a major problem in the application of superconducting technology to storage rings and accelerators. In recent years new choices of cavity geometries which inhibit multipacting have been successfully applied to the construction of superconducting accelerator structures. The problem remains, however, of decreasing or eliminating the effects of multipacting in parts of the structures for which the geometry cannot be significantly changed, such as in higher-order-mode couplers. In these cases the suppression of multipacting can be achieved by coating the surfaces of interest with a material which must have both a low secondary electron emission (SEE) coefficient and low RF losses, in order to maintain the original high unloaded Q of the cavity. Materials such as NbC, NbN, TiC and TiN seem to be good candidates for this purpose. They are good electrical conductors and possess rather high superconducting transition temperatures (1).

TiN is routinely used at SLAC as a proven anti-multipactor coating for inter-cavity coupling slots, RF windows and RF coupling loops on normal conductor surfaces. Preliminary surface physics studies on this material indicated that the as-deposited films exhibited low SEE yields, but exposure to air caused the SEE yields to increase so much that such films would appear useless as anti-multipactor coatings. To explore the apparent contradiction between experiment and practice, those conditions were examined which might lead to an in-situ lowering of the SEE yield. One such condition is electron-bombardment of the TiN-coated surfaces during initial running of RF devices.

2. Experiment

The experimental apparatus consisted of a stainless steel UHV analysis chamber linked to a process system chamber via magnetically coupled sample transfer mechanism (Figure 1). The pressure was typically 2×10^{-10} Torr in the analysis chamber and 1×10^{-9} Torr in the process chamber.

A Vacuum Generators CLAM 100 XPS unit controlled by an LSI-11 com-

puter was used to collect the Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) data using electron counting techniques. The secondary electron emission (SEE) yield data were collected using an electron beam at normal incidence, a programmable high voltage power supply and an electrometer which were also under computer control (Figure 2).

The samples were single crystal Nb discs of unknown orientation, 1.6 cm diameter x .5 cm thick cut from 2500 K outgassed low-Ta rods, mechanically polished with .5 μ m diamond paste and electropolished in 10% HF - 90% H₂SO₄ solution which removed approximately 50 μ m of Nb surface.

The discs were sputter-cleaned and the various films were sputter-ion deposited using a Kaufman-type (2) ion source. The films were deposited to a thickness of 140A as determined by using a quartz-crystal thickness monitor, this being the thickness of the TiN coatings used successfully at SLAC. Immediately after deposition the samples were transferred to the analysis tank for the SEE, AES, and XPS measurements.

The SEE measurements were done using a retarding voltage method in which a 1.5 KeV electron beam with a current of 2 nA strikes the sample whose potential is varied from -50 to -1450 volts in 10 volt steps. The current flowing through the sample was measured at each retarding voltage by an electrometer, and the total secondary yield σ was calculated using: $\sigma = 1 - (\text{target current} / \text{primary current})$.

The AES measurements were taken using a electron current of 50 nA rastered over approximately .25 cm² of the sample. The analyzer was operated in the constant retard ratio (CRR, energy resolution $\sim$ 1%) mode for the AES measurements.

The XPS data was collected using a Mg anode bombarded with 12 KeV electrons at 20 mA. The VG analyzer was operated in the constant analyzer energy (CAE, energy resolution $\sim$ 0.75 eV) mode with a pass energy of 20 eV. Photoelectrons were collected from .17 cm² sample area, chosen to fall within the area dosed in the electron beam exposure experiments to be described later.

After the data on the as-deposited films was collected, the samples were

moved to a loading chamber where they were exposed to room air (22°C, 50% RH) at atmospheric pressure for one hour. The loading chamber was then evacuated and the samples were transferred back to the analysis tank for characterization as described above.

The electron beam exposures were accomplished using an energy of 1067 eV and a current of 400 nA rastered over .98 cm² for the 140A TiN and NbC and 80 nA rastered over .37 cm² for the 15A TiN, 140A NbN, 140A TiC films and the oxidized uncoated Nb surface.

3. Results

When referring to the accompanying diagrams, (a) refers to the as-deposited films; (b) refers to the films exposed to air; and (c) refers to the results after electron beam bombardment. Data is also presented for the clean Nb substrate and its air oxidized surface. The plots are offset vertically with respect to each other for clarity.

The SEE measurements indicate that the lowest σ occurs on the as-deposited films. In some cases σ remains below one over the entire incident energy range 50-1450 eV. After exposure to air σ rises substantially above the initial value. Subsequent electron beam bombardment serves to reduce σ , in some cases to nearly the value obtained for the as-deposited film.

The AES measurements of the as-deposited films show the elemental compositions of the surfaces of the films. In addition to the primary elements of the deposited materials small amounts of oxygen are seen on some of the layers. This is probably due to H₂O desorption from the chamber walls during sputter deposition. After exposure to air an increase in the oxygen peak area is noted along with a small increase in the carbon level. Changes in the structure of the primary AES peaks will reflect changes in the chemical composition of surface layers in our data. After electron beam bombardment, only small changes in the AES spectra are seen, compared to the oxidized overlayers, indicating that the relative amounts of each element are largely unaffected. Retrieving information

about chemical states is difficult due to the nature of the AES technique and quantitative analysis of these spectra was therefore not undertaken.

The XPS data gives more easily extractable information about the chemical states present in the films but probes to a greater depth than AES. After deposition, XPS shows primarily the material sputtered onto the Nb discs with some films incorporating small amounts of oxides (again, due to H_2O desorbed from the chamber walls during sputter deposition). After exposure to air the amount of oxide present in each material rises significantly with a concomitant decrease in the primary species. After electron beam bombardment XPS shows that the oxide levels are slightly reduced by the bombardment.

In addition to XPS, AES and SEE, we have made some electron-induced-desorption (EID) measurements of the oxidized layers on Nb and NbN/Nb. O^+ emission is observed whose desorption rate increases with e-beam exposure, in agreement with the observations of others (3). This rate increase is due to a rise in the surface concentration of weakly bound surface oxygen, created during reduction of the Nb_2O_5 to sub-oxides by electron bombardment.

4. Discussion

4.1 CLEAN Nb

The results presented here for clean sputtered Nb are similar to those which we have obtained for furnace-cleaned Nb (2300K, 21 hrs. at 3×10^{-10} Torr). Sputtered surfaces can always be made C and O-free whereas we have observed very small amounts (<5% of a monolayer) of O on all furnace-cleaned samples. This appears to be due to dissolved O from the bulk diffusing to the surface during heating. For both types of cleaning, however, we obtained essentially identical XPS, AES and SEE data.

4.2 TRANSITION METAL CARBIDE AND NITRIDE OVERLAYERS

Using these materials as secondary electron suppressors on Nb would seem to be an ideal choice. They are excellent electrical conductors, have low secondary emission coefficients and high superconducting transition temperatures

(1). From the data, we see that σ is quite low for these as-deposited overlayers on Nb and that the electron backscatter contribution at higher primary energy is smaller than that for uncoated Nb (compare for example, σ for clean Nb and 140Å TiN/Nb). At this time, the mechanism for reduced secondary emission in transition metal carbides and nitrides is not understood.

4.3 OXIDIZED NB AND OXIDIZED OVERLAYERS

Upon exposure to air (and pure oxygen, as well, we have found), the bare Nb surface and its overlayers form thin surface oxides at the exposures used in this experiment. For instance, clean Nb oxidizes to about 10Å (4) and we expect that the overlayers oxidize to a similar depth, for example, the 15Å TiN overlayer does not quite fully oxidize, (i.e., significant TiN concentrations are present in the Ti core level spectra) according to the XPS results. XPS shows the presence of Nb₂O₅ (as well as sub-oxides) for oxidized Nb, NbN and NbC. TiO₂ is observed for TiN and TiC oxidized overlayers. AES (which probes a shallower depth) confirms these observations.

The SEE yield shows a large increase upon oxidation, a result which is expected for bulk oxides and which is observed here for very thin oxides. Surface charging of <1eV has been observed in thin MgO layers (5) and oxidized Nb before (6), so it is reasonable to believe that charged holes can be generated in the oxidized layer through pair production. The presence of this positively charged layer results in a drop of the work function (7) and the presence of an accelerating field across the oxide (4), either of which results in increased secondary electron emission thereby accounting for the observed increase in σ upon oxidation.

4.4 ELECTRON-BOMBARDMENT

Continued electron-bombardment of the oxidized overlayers produces damage in the form of broken bonds, reduced oxides, excited species, mobile and immobile holes, etc. This is reflected in O⁺ being electron-desorbed as described in the EID results above. The desorbing O⁺ (and possibly neutral CO and CO₂) is also observed as a small change in the XPS O signal and AES C and O signals. The SEE yield, however, shows a large change in value as a result of this

bombardment. Electron-bombardment generated damage in the oxide results in a good conducting layer (i.e. the oxide turns metal-like), and the surface charge, which sustained the increased SEE yield observed before bombardment, vanishes; σ drops back toward its value for the unoxidized surface. In fact, visible discoloration of such a bombarded area has been observed by others (3). Ultimately, with larger electron exposures than those used here, one would expect the appearance of free metal in the oxide layer. This has also been observed (3).

5. Conclusions

Although clean Nb has a SEE yield low enough to be useful for the construction of RF cavities, the native oxide which forms upon exposure to air increases the SEE yield enough to cause multipacting to be a major problem. It is therefore useful to coat Nb structures with materials capable of reducing the effects of multipacting, and which preserve the superconducting properties of the clean Nb surface.

Materials such as NbC, NbN, TiC and TiN, as-deposited, have SEE yields low enough to minimize multipacting effects. Exposing these coatings to air causes a rise in the SEE yields and would apparently make them unsuitable for use in RF cavities.

We have shown, however, that electron bombardment with doses of less than 10^{18} cm^{-2} reduces the SEE yields to values approaching those of the as-deposited films. We conclude that the in-situ electron bombardment, which occurs during rf device processing and is several orders of magnitude greater than that used in our experiments, serves to reduce the effective SEE yield and thereby may cause substantial reduction in multipacting in coated RF cavities.

6. References

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7. Figure Captions

1. Coupled surface analysis - process systems.
2. Total secondary electron emission (σ) measurement schematic.
- 3.-20. σ vs. Ep, XPS and AES spectra for clean, oxidized and electron bombarded surfaces of Nb (3-5), 15A TiN/Nb (6-8), 140 A TiN/Nb (9-11), 140 A TiC/Nb (12-14), 140 A NbN/Nb (15-17), 140 A NbN/Nb (18-20):
 - (a) As cleaned or deposited
 - (b) oxidized at 1 atm, 3600 sec.
 - (c) electron bombarded (dose rate and total dose indicated)

FIGURE 1.

TOTAL SECONDARY YIELD MEASUREMENT

FIGURE 2.

Dose Rate = $1.58 \times 10^{12} \text{cm}^{-2} \text{sec}^{-1}$

Total Dose = $6.1 \times 10^{17} \text{cm}^{-2}$

FIGURE 3.

FIGURE 4.

FIGURE 5.

FIGURE 6.

FIGURE 7.

FIGURE 8.

FIGURE 9.

FIGURE 10.

FIGURE 11.

FIGURE 12.

FIGURE 13.

FIGURE 14.

Dose Rate = $1.31 \times 10^{12} \text{cm}^{-2} \text{sec}^{-1}$

Total Dose = $1.7 \times 10^{17} \text{cm}^{-2}$

FIGURE 15.

FIGURE 16.

FIGURE 17.

Dose Rate = $2.45 \times 10^{12} \text{cm}^{-2}\text{sec}^{-1}$

Total Dose = $3.25 \times 10^{17} \text{cm}^{-2}$

FIGURE 18.

FIGURE 19.

FIGURE 20.