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Detection of surface nitrogen in high-T_c Nb_3Ge films by Auger analysis

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Auger electron spectroscopy was applied to Nb_3Ge films that possessed T_c's above 20 K. The surface composition was determined from the Auger spectra. A considerable amount of nitrogen was detected on the surface. This amount, which varied by a factor of 3 across the surface, was 100 times higher than the nitrogen concentration in the film. The discrepancy is tentatively assigned to the effect of argon-ion sputter cleaning prior to the Auger measurements.

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I. INTRODUCTION

Thin films of Nb_3Ge made by sputtering a Nb_3Ge compound electrode in an argon atmosphere have the highest known superconducting transition temperature (T_c), ~23 K.[1,2] The conventional method of quenching arc-melted Nb and Ge produces material that superconducts at temperatures always less than 17 K. Both chemical vapor deposition[3] and electron-beam coevaporation[4] of Nb and Ge are capable of producing materials with $T_c > 21$ K, although their T_c's are still below those of the sputtered films.

The presence of sputtering gases in these high-T_c films is a possibility that should not be overlooked. Because the small quantity of material available makes analysis difficult, we have carried out Auger analysis on the surface of the film. The Auger method can detect all elements (except hydrogen) but is particularly sensitive to low atomic weight elements. Complete analyses of the bulk of these high-T_c films by x ray and helium-ion Rutherford back scattering, which is more sensitive to heavier elements, were reported by Testardi *et al.*[5] The bulk N content in their work was also found to be < 1% by a nuclear reaction technique specific for nitrogen. Our experiments determine only the surface composition which, of course, may be appreciably different from the bulk.

By the combination of Auger electron spectroscopy and argon-ion sputtering, the surface composition of Nb_3Ge films was determined as a function of sputtering time. The sample was sputtered at 5×10^{-5} Torr for 10 min and examined by Auger spectroscopy in the same argon atmosphere. When examined in this manner, a considerable amount of nitrogen, in addition to niobium and germanium, seems to exist on the surface of such films. Oxygen and carbon, which are the common surface impurities of Nb, are also present. The nitrogen to Nb atomic ratio on the surface can be as high as 0.12—0.3, the latter number being 100 times higher than the result obtained for the bulk of the same film by means of the nuclear reaction technique.[3] In this paper, attempts will be made to explain the large discrepancies observed here, and describe the conditions that preceded the measurement.

The bulk composition of an alloy is commonly assumed to be the same as that of the surface layer (~20 Å) probed by the Auger method. However, in numerous cases,[8,9] the surface composition can be markedly different from that of the bulk. The difference depends on the preparation and treatment of the surface before measurement. For example, in a simple binary alloy such as Cu-Ni (coins) the surface can be either Ni or Cu rich depending on previous treatments. The differences in sputtering yield per unit argon ion for Cu and Ni can be used to explain the Ni-rich surface[10] and the differences in binding energies or heats of vaporization can be used to explain the Cu-rich surface.[11] The interpretation of the surface composition of complex alloys with very dissimilar atoms has to be viewed with extreme caution.

II. EXPERIMENTAL RESULTS

The experiment was performed in an all stainless-

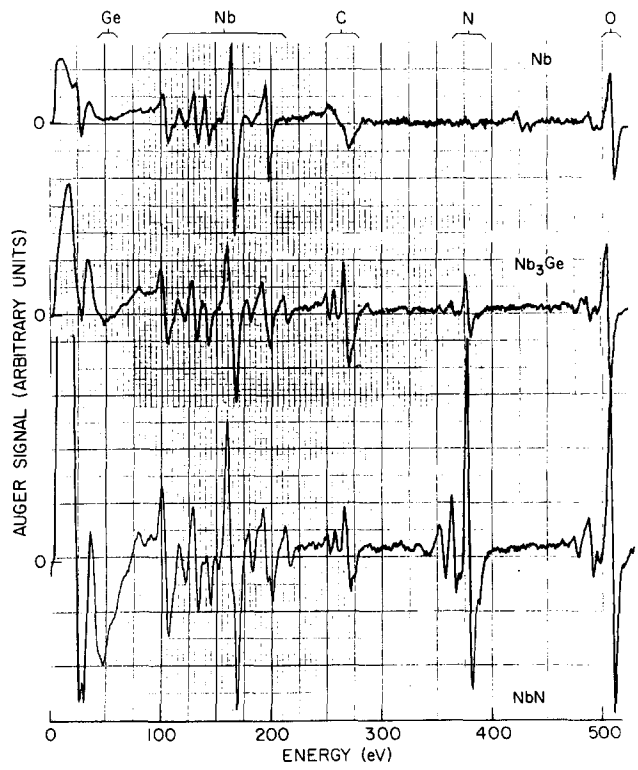

FIG. 1. The energy distribution of Auger electrons excited by 3-keV electrons. The top curve indicates a Nb sample. The middle curve is Nb_3Ge (800/5). The bottom curve is niobium nitride. The location of lines identifies the presence of individual elements which are labeled on the top of this figure.

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steel vacuum system that contains a high-precision double-cylindrical Auger spectrometer, model No. 15-25G, and a sputtering gun, model No. 04-161 (both manufactured by Physical Electronic Industries), a quadrupole mass spectrometer, model No. 1200 (manufactured by Electronic Associates Inc.), and a high energy electron diffraction system (manufactured by Vacuum Generator, U.K.). The Nb_3Ge (sample No. 800/5) film ($T_c = 20$ K) was made by sputtering a Nb_3Ge electrode onto a hot sapphire substrate[2] in an argon atmosphere. The presence of nitrogen can be detected by two independent methods. The first method is the observation of nitrogen peaks in the Auger spectrum of the film. It is found that the nitrogen to niobium ratio is independent of the amount of other surface impurities such as oxides and carbides. The second method is the evolution of nitrogen when the film is bombarded by 2-keV argon ions from the sputtering gun. The nitrogen appears as N_2^+ (mass 28) and N^+ (mass 14) ions in the mass spectrometer. The determination of the N to Nb atomic ratio is made quantitative by comparing the Auger and mass spectrometer data of the Nb_3Ge sample with that of a NbN foil ($T_c = 13.5$ K).

Figure 1 shows the Auger data of the samples. The top curve is the spectrum of a pure Nb foil which has been heated to high temperatures (2000 °C). The presence of carbon and oxygen is representative of the purity of the sample. Sputter cleaning of an oxidized Nb foil at room temperature produces an identical curve except that the oxygen peak is reduced by half. Oxygen was especially difficult to eliminate from the Nb surface at room temperature even though the residual pressure remained at 9×10^{-11} Torr. The Nb curve is in agreement with the data of previous workers.[12] The transition metal carbides have three carbon lines at 253, 260, and 271 eV. The Auger spectrometer is especially sensitive to low-atomic-number elements which are characterized by sharp transitions and high Auger electron yield. In order to compare with the majority of past measurements 3-keV electrons are used to produce the Auger electrons. The Nb_3Ge sample is shown as the middle curve. This particular sample possessed one of the highest N contents. The Nb characteristic lines are essentially the same. The 215-eV dip is an argon line originated from the sputter-cleaning process because the line is observed in both Nb_3Ge and NbN samples. The presence of Ge should generate two dips at 47 and 52 eV which overlap with weak Nb lines there. Positive identification of Ge is made at the strong 1147-eV line which is not shown on this scale. The lines of Nb in the compound appear broader when compared with pure Nb but qualitatively maintain the same shape. The strongest line of Nb decreases by about 2 eV in the compound. The instrument resolution is about 0.5 eV. Nitrogen lines at 380 eV are quite prominent on this curve. The sample surface was cleaned by 2-keV argon ion bombardment at 5×10^{-5} Torr argon pressure before this trace was taken in the same argon atmosphere. The argon ion beam was generated by the sputtering gun and was normal to the substrate. The current density was about 15 $\mu A/cm^2$. Annealing to 500 °C does not produce any change in the spectrum. Because of the small sample surface available, no diffraction pattern was generated by the 40-keV electron beam. Higher annealing temperatures, which may cause film decomposition, were not tried on the Nb_3Ge samples. Argon ion bombardment at room temperature cannot remove all the oxygen from the niobium surface. The lower curve shows the spectrum of a NbN foil that superconducts at 13.5 K. Room-temperature argon ion bombardment was again used to clean the sample surface which was not annealed. During the argon bombardment the combination of a mass spectrometer and a hot-filament ionization gauge were used to monitor the change of the N_2 partial pressure with time.

The following tests are used to establish that nitrogen is contained in the Nb_3Ge film rather than picked up from the atmosphere during or between measurements. The concentration of nitrogen is measured by the peak-to-peak height $N_{p\text{-}p}$ at 380 eV divided by the peak-to-peak height of niobium $Nb_{p\text{-}p}$ at 179 eV. The concentration of oxygen at 520 eV and carbon at 273 eV are determined relative to the niobium in the same way. Before any argon-ion sputter cleaning, the oxygen peak-to-peak $O_{p\text{-}p}$ is 14 times larger than $Nb_{p\text{-}p}$. The asymmetric carbon peak C_p is eight times larger than $Nb_{p\text{-}p}$. When the film is subject to argon bombardment, the $O_{p\text{-}p}/Nb_{p\text{-}p}$ and $C_p/Nb_{p\text{-}p}$ ratios decrease with increasing time but the $N_{p\text{-}p}/Nb_{p\text{-}p}$ ratio remains nearly constant and increases slightly with time. The ratios $O_{p\text{-}p}/Nb_{p\text{-}p}$ and $C_p/Nb_{p\text{-}p}$ reduce to one-tenth of their original values after 12 h of cleaning but the $N_{p\text{-}p}/Nb_{p\text{-}p}$ ratio increases slightly in the same period. The sample was then exposed to air and T_c determined to be 20 K. After putting the sample back in the vacuum system, both carbon and oxygen concentrations have increased by a factor of 5 but the range of N to Nb ratio remains between 0.1 and 0.3. The rapid formation of oxide on the Nb surface at room temperature inhibits the formation of nitrides.[13] Argon ion bombardment again removes the oxides and carbides which exist on the surface. The $N_{p\text{-}p}/Nb_{p\text{-}p}$ ratio decreases from 0.4 to 0.2 during the first hour of sputtering and increases from 0.2 to 0.4 in the next 5 h of sputtering. In the same 6 h $O_{p\text{-}p}/Nb_{p\text{-}p}$ decreases monotonically from 7 to 0.8 and $C_p/Nb_{p\text{-}p}$ from 1.8 to 0.35.

The middle curve of Fig. 1 indicates the surface composition at one point after the 6-h sputtering period. It is also possible to observe directly the formation of surface oxides and carbides inside the vacuum system. This is presented in Fig. 2 which depicts the evolution of the middle curve in Fig. 1 with time after switching off the sputtering beam. In 3 h, the oxygen level increases by a factor of 2, the carbon signal appears to increase slightly, but the nitrogen level remains unchanged within experimental error.

The nitrogen concentration can be determined quantitatively by using the NbN data in Fig. 1 as a calibration standard. The data gives $N_{p\text{-}p}/Nb_{p\text{-}p}$ between 1.2 and 1.4 in the NbN Auger spectrum. If we assume that the 1 to 1 atomic ratio is retained on the NbN surface, the N/Nb atomic ratio is between 0.28 and 0.35 on the surface of the Nb_3Ge film at the point chosen in Fig. 1.

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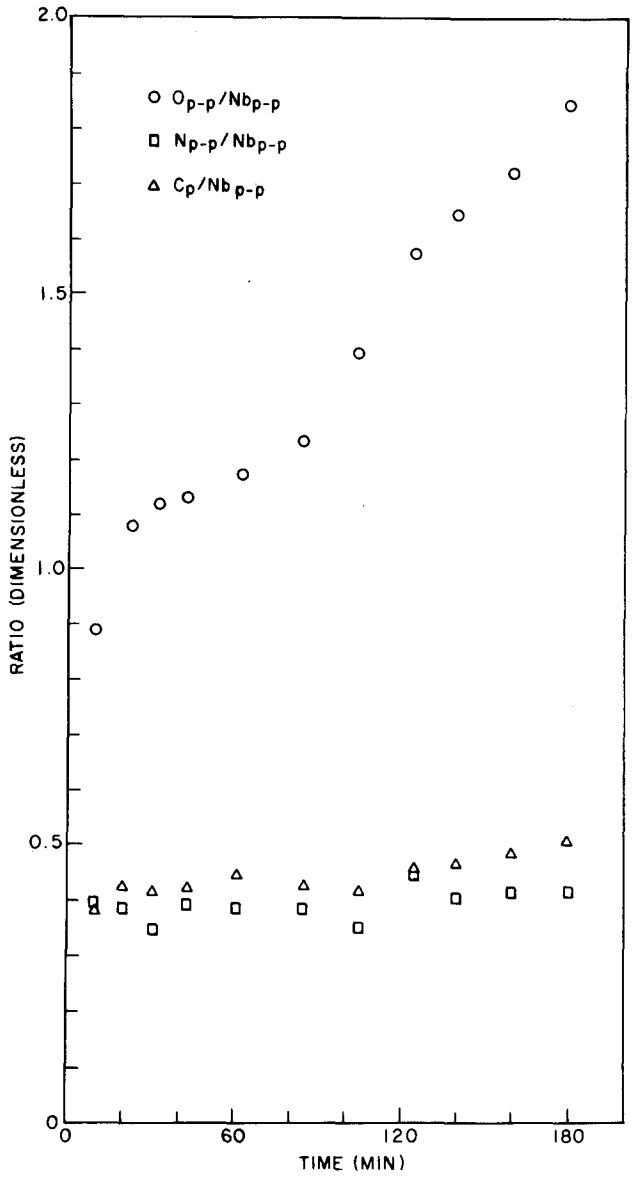

FIG. 2. The evolution of the middle curve in Fig. 1 with time. The peak heights of O, N, and C, divided by the Nb peak height, are plotted as a function of time. Time zero signals the end of argon ion bombardment.

However, bulk measurements on the same film showed $N/Nb < 0.01$.

The N to Nb atomic ratio can also be determined directly from the middle curve of Fig. 1 independently of the NbN calibration curve. This is done by comparing the Auger peak-to-peak heights of Nb and N and making use of the "inverse Auger sensitivity factors", α.[14] These correction factors are known for N ($\alpha = 1$) and Ge ($\alpha = 3.2$), but were not determined for Nb. By comparing the Auger signal of Nb and Ge in the second Nb_3Ge sample that we measured (sample No. 750/3) and assuming a stoichiometric Nb_3Ge surface composition, we can estimate the α of Nb to be 1.3 at 168 eV. The N to Nb atomic ratio of the middle curve in Fig. 1 equals $N_{p-p}(1.3 \times Nb_{p-p}) = 0.31$. The disagreement between this number and the bulk concentration will be discussed in Sec. III.

Instead of relying on the stoichiometric composition of an alloy surface, the α of Nb can further be checked by the Auger spectrum of a thermally oxidized Nb surface. On such a surface the measured O_{p-p}/Nb_{p-p} equals 3.32. Assuming the O/Nb atomic ratio is 2.5, the α of Nb equals to $\alpha(O) \times 3.32/2.5 = 1.33\alpha(O)$. From Ref. 14 $\alpha(O)$ was known to be unity. As a result $\alpha(Nb) = 1.33$ which agrees with the values obtained from the other two Nb alloys.

The nitrogen concentration can also be estimated from the mass spectrometer, which gives the increase of the nitrogen partial pressure during sputtering. The nitrogen generation rate is 0.16×10^{-6} Torr/min for the high-T_c film and 0.8×10^{-6} Torr/min for NbN foil. The rate was measured after the titanium sublimation pump was saturated with nitrogen from the film. This gave the N to Nb ratio as 0.2. There is some uncertainty here due to the relative sizes of the sputtered areas. No oxygen was observed during the sputtering period. This is probably because the whole Nb-oxide molecule was sputtered away without decomposition. Part of the Nb nitrides decompose under ion bombardment, causing the increase of the partial pressure of nitrogen in the surrounding argon atmosphere. We have also sputtered an anodized tantalum surface, from which 500 Å of Ta_2O_5 was removed from a large area without generating any trace of nitrigen or oxygen in the vacuum system. As a check on whether the nitrogen originates from the sample holder or the surroundings, we have ion-bombarded Nb foils, Nb crystals, and sputtered Nb films that did not show any nitrogen peaks detectable by Auger spectroscopy. In no case could the oxygen lines be completely removed from the sample spectrum, even though the oxygen lines were made 10 times smaller than the original untreated surface.

The nitrogen concentration was found to be nonuniform on the surface of both the Nb_3Ge film and NbN foil. This observation is plotted as a histogram in Fig. 3 for all Auger spectra taken. The numbers measured are shown inside the boxes. No attempt will be made to explain the large spread of numbers. The sampling area of Auger spectra is thought to be $\sim 10^{-5}$ cm^2. The

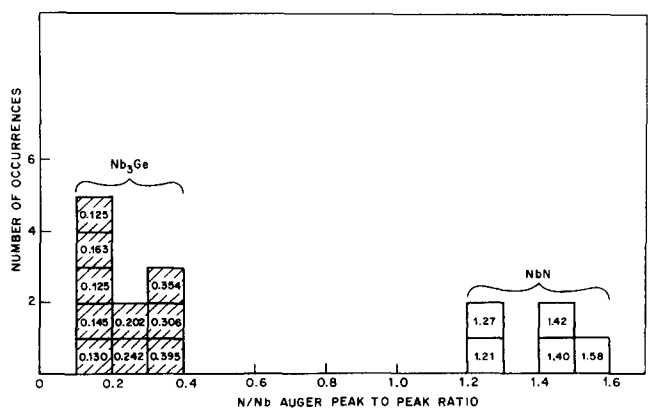

FIG. 3. A histogram which indicates the spatial distribution of nitrogen on Nb_3Ge (800/5) and NbN.

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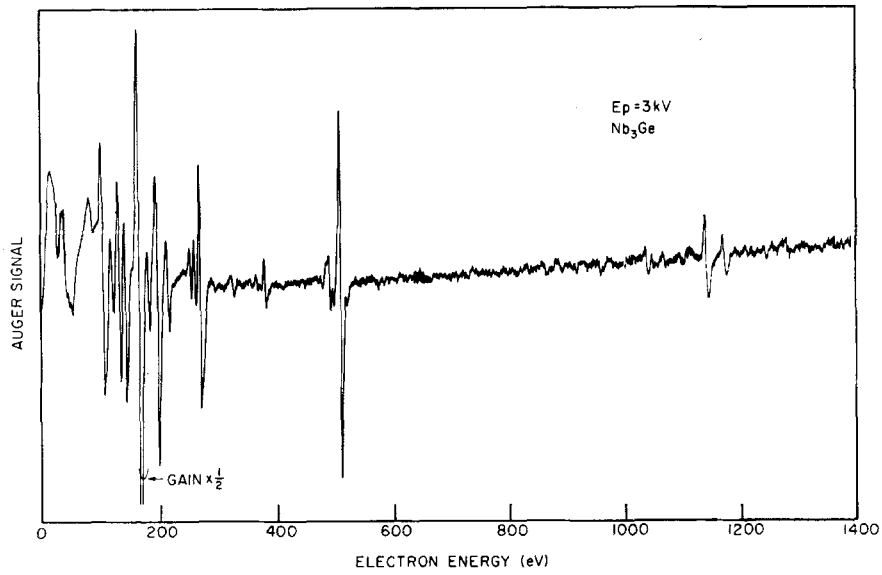

FIG. 4. The Auger spectrum of a second high-T_c Nb_3Ge (750/3°) film with less nitrogen.

results may be influenced by the sputter-cleaning process from the ion gun.

Another Nb_3Ge film (sample No. 750/3) with $T_c \sim 20$ K was also measured. The Auger spectrum shown in Fig. 4 indicates a lower nitrogen content at this point in the sample. In this curve, we can clearly identify the Nb line at 168 eV, the N lines at 380, and the Ge lines at 1147 eV. Carbon and oxygen lines are also present as impurities. From this curve the N/Nb atomic ratio was determined to be 0.07, and the spread of values in this film was from 0.05 to 0.07.

Both Nb_3Ge films were analyzed by Rutherford backscattering and nuclear reaction techniques[3] after the Auger measurement. The bulk N/Nb ratios are 0.004 and 0.003, respectively. The Auger measurement was then repeated on the same samples. The atomic ratio $N_{p-p}/(1.3\times Nb_{p-p})$ was reduced in both cases, from 0.3 to 0.08 and from 0.07 to 0.04, respectively; and the minimum achievable C_{p-p}/Nb_{p-p} was increased from 0.5 to 1. In the meantime, the T_c's of the samples were reduced to 18.5 and 17.7 K, respectively. This may be due to the destructive nature of the nuclear reaction testing techniques and the sensitivity of T_c's to damage. Two possible explanations for the differences in surface composition and bulk composition will be presented in Sec. III.

The Nb_3Ge sample was observed to have a large N/Nb ratio even before the argon-ion sputter-cleaning process began. The ion bombardment reduced the carbon and oxygen peaks but was incapable of reducing the nitrogen concentration on the surface. Both Nb_3Ge and Nb do not react with N_2 in the air. The present study indicates that the imbedded nitrogen in the film tends to accumulate on the surface.

III. DISCUSSION

The disagreement between the nitrogen content obtained from the Auger analysis and the nuclear reaction method can be understood in two ways. The first one relies on the dynamic equilibrium condition achieved during ion bombardment.[10] The difference in the sputtering yield r and s (atoms/ion) of a binary alloy NbN will yield the following condition $n/m = rb/sa$, where n and m are the surface concentrations (at.%) of N and Nb and b and a are the bulk concentrations (at.%) of N and Nb. From the lower Auger curve of Fig. 1, and after correction for the inverse Auger sensitivity factors, the surface concentration is close to NbN, or $n/m \sim 1$. As a result, the sputtering yield r and s is about the same for Nb and N. If r and s remained equal in Nb_3Ge, the nitrogen surface concentration would be the same as the bulk concentration which is contrary to experimental observations. In order to produce a nitrogen-rich surface, the sputtering yields of both Nb and Ge would have to be much greater than that of nitrogen. When bombarded by 0.4-keV argon ions, the sputtering yields of Nb and Ge are 0.5 and 0.9 atom/ion.[15] The sputtering yield varies a lot across the Periodic Table; it has a low value of 0.2 atom/ion for carbon and a high of 3 atoms/ion for Ag. It is possible that the released ionized nitrogen from the part of Nb_3Ge which has been etched away during ion bombardment reacts with the active exposed Nb surface to form NbN. NbN can be produced under similar conditions by sputtering Nb inside a nitrogen- containing argon atmosphere.[16]

We can calculate the partial pressure of nitrogen when it was released from the film. There are approximately 10^{15} nitrogen atoms in a 500-Å-thick Nb_3Ge film which contain 0.005 nitrogen over an area of 0.5 cm^2. When we etched away this amount of film by ion bombardment, the total released nitrogen would contribute 10^{-6} Torr of nitrogen to a vacuum system of 22 liters. The actually released nitrogen is more than this. The origin of this discrepancy was not understood

The thermal diffusion rate of both N and O through Nb metal is exceedingly slow at 500 °C and below.[17] As a result the surface concentration of N can remain 100 times higher than the bulk concentration as long as 10^4 days even at 500 °C. The grain boundaries present in thin films tend to speed up the diffusion process.

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A second alternative explanation involves the thermodynamic equilibrium achieved during sputtering and annealing.[11] Williams and Nason[11] calculated the surface concentration of a binary alloy where the binding energies between nearest and second nearest neighbors were included. The results of this calculation indicated that the alloy surface would be enriched with the component having the smallest heat of sublimation H (or the highest vapor pressure at a fixed temperature). The surface concentration of the other component is $\sim\exp(-\Delta H/RT)$ if $\Delta H \gg RT$, where ΔH is the difference between the heat of vaporization of the two components. The H's for N_2, Ge, and Nb are 1.3, 80, and 175 kcal/mole, respectively. One would expect the surface to be almost completely covered with N under thermodynamic equilibrium at room temperature, if nitrogen has sufficient affinity to Nb surface to keep it from being removed by the pump. A tendency to form strong surface bonds as in some oxides could override the heat of sublimation, so that the oxide-forming component would segregate to the surface. This is indeed observed when the sample is exposed to air, which causes a complete coverage of stable Nb oxides over the entire surface.

The surface composition of a superconductor can affect high-frequency ac impedance and electron tunneling characteristics. The presence of niobium nitride ($T_c \sim 17.8$ K)[6,16] on the surface when treated by sputter cleaning can drastically alter the surface superconductive properties of the high-T_c film. Auger studies on samples of this type produce useful but sometimes puzzling results. The purpose of this work is to provide information that may be useful to the study of other properties of the Nb_3Ge films.

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