Modification of niobium film stress by low-energy ion bombardment during deposition

J. J. Cuomo, J. M. E. Harper, C. R. Guarnieri, D. S. Yee, L. J. Attanasio, J. Angilello, and C. T. Wu

IBM Thomas J. Watson Research Center, Box 218, Yorktown Heights, New York 10598

R. H. Hammond

Hansen Physics Laboratory, Stanford University, Stanford, California 94305

(Received 1 October 1981; accepted 21 December 1981)

The effect of ion bombardment on film stress was studied by evaporating Nb thin films in the presence of a controlled ion beam from a Kaufman ion source. Films were deposited at 4 Å/s by electron-beam evaporation with ion bombardment over the energy range 100–800 eV, at ion current densities of 0.001 to 1.1 mA/cm^2. Film stress was measured by an x-ray bending-beam technique on Si substrates. Stress values were found to depend strongly on both ion flux and sample temperature. For films deposited at 400 °C, film stress is tensile in the absence of ion bombardment. Increasing argon ion flux causes a change toward compressive stress, in some cases passing through zero. For films deposited at room temperature, film stress is compressive in the absence of ion bombardment, due to incorporation of oxygen. Argon ion bombardment causes a change toward tensile stress, correlating with an improvement in film purity by preferential resputtering of oxygen. With 100 eV argon ions, an ion-to-atom ratio of only 3–10 % is sufficient to cause reversal of the sign of film stress in most cases. Results are interpreted as a combination of cleaning by resputtering and annealing or compacting the film microstructure. In addition, nitrogen ion bombardment is shown to produce superconducting NbN films with a superconducting transition temperature up to 14.5 K.

PACS numbers: 61.80.Jh, 68.60. + q, 73.60.Dt, 74.70.Lp

I. INTRODUCTION

Intrinsic stress in thin films can be high enough to cause severe problems in many materials applications. Typically, evaporated films of refractory metals retain high tensile stress,[1] while sputtered films may have tensile or compressive stress, depending on the nature of energetic particle bombardment. Studies by Thornton and Hoffman[2] and Hoffman and Gaerttner[3] indicate that energetic neutral or ion bombardment of a film during growth causes a change toward compressive stress. This mechanism may cancel the tendency toward tensile stress exhibited by films deposited under conditions of low atom arrival energy.

In this paper, we report the effect of low energy ion beam bombardment on the intrinsic stress of electron-beam-evaporated Nb films. A Kaufman ion source[4] was used to provide a controlled argon ion flux of 100–800 eV, at 0.001 to 1.1 mA/cm^2, during deposition of Nb at rates of 4–10 Å/s. Substrate temperatures were varied from 30 to 400 °C. Film stress was measured from the curvature of the substrate by an x-ray bending beam technique.[5] Resistivity, superconducting transition temperature, and composition were also measured on selected samples.

Stress values were found to depend strongly on substrate temperature and degree of ion bombardment. Samples deposited at 400 °C with no ion bombardment were under high tensile stress (up to 10^{10} dyn/cm^2), resulting in adhesion failure in films thicker than several thousand Å. With increasing ion flux, the stress changed toward compressive values. With 100-eV ar ions, an ion-to-atom arrival rate ratio of only 3–10 % was typically sufficient to cause compressive stress. This behavior is similar to that observed by Hoffman and Gaerttner[3] with Cr films, except that in the present study the stress transition is obtained with very low energy ions.

However, with substrate temperatures below 100 °C, the trend is reversed. Samples deposited at room temperature with no ion bombardment are under compressive stress, due to incorporated impurities, primarily oxygen. With increasing ion flux at 100 eV, the film stress changes toward tensile values at low values of ion flux. Electron microprobe, Rutherford backscattering, resistivity, and transition temperature all indicate a cleaning of the film by preferential resputtering of oxygen. At intermediate substrate temperatures, a superposition of these two trends results in a peak in tensile stress as a function of ion flux. For these intermediate substrate temperatures, the main effect of increasing the ion flux is to improve the purity of the film. This results in increasing tensile stress. Once a critical purity is reached, the main result of increasing ion flux is to decrease the stress towards compressive values. This appears to be caused by changes in film microstructure, and is under further investigation.

Several mechanisms have been identified which lead to tensile stress in evaporated thin films.[1] Low atom mobility is the key factor which allows voids and grain boundaries to remain in the growing film structure. These defects exert an attractive interatomic force which results in a net tensile stress. Incorporation of interstitial impurities normally produces compressive stress due to the force exerted by the addi-

tional atoms.[6] In copper, an oxygen concentration of only a few atomic % leads to a stress reversal from tensile to compressive.[6] With a reactive metal such as Nb, oxygen is easily incorporated when the deposition rate is low relative to the arrival rate of residual water vapor or oxygen in the system.[7,8] For example, an O_2 partial pressure of 10^{-8} Torr during deposition provides an impingement rate high enough to incorporate about 2% oxygen in a Nb film deposited at 4 Å/s, assuming unity sticking coefficient. Increasing the substrate temperature to several hundred °C reduces the sticking coefficient, with a corresponding improvement in film purity.[7,8]

Ion bombardment during deposition has been shown to increase the purity of sputtered films[9] by preferential resputtering of adsorbed impurity atoms. Additional effects on film stress have been attributed to the direct transfer of momentum to the film atoms. The term "ion peening" has been invoked by Hoffman and Gaerttner[3] to explain the trend to compressive stress with increased flux and energy of energetic particles in sputtering and in evaporation under ion bombardment. In addition, Hirsch and Varga[10] propose the mechanism of "ion-beam annealing" in reducing the high tensile stress of evaporated Ge films. There is strong evidence that ion bombardment has a direct effect on film stress through the modification of microstructure by momentum transfer, and additional secondary effects through the cleaning of the film by resputtering of impurities. The stresses induced both by ion bombardment and impurity concentration are modified by the substrate temperature.

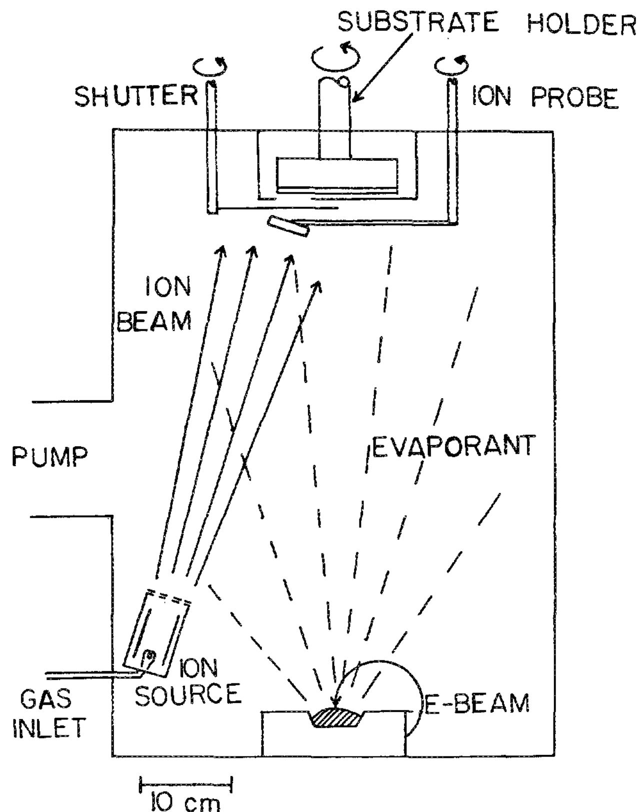

FIG. 1. Schematic diagram of deposition system, showing electron-beam-heated Nb crucible, ion source, and multiple-position substrate holder.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

Substrates for stress measurements were rectangular strips of single crystal Si ($23 \times 2.8 \times 0.2$ mm), coated on both sides with about 500 Å of Si_3N_4. The initial radius of curvature of each strip was measured by an x-ray bending beam technique.[5] Substrates were cleaned with ultrasonic detergent, deionized water, alcohol, and nitrogen drying, and mounted with spring clips to a copper plate holding six substrates for sequential deposition.

B. Film deposition

A schematic diagram of the sample chamber is shown in Fig. 1. The chamber is pumped with a 6-in-diam diffusion pump with a LN_2-cooled Ti sublimation pump. Initial base pressure was typically $4–8 \times 10^{-8}$ Torr in the sample chamber prior to deposition. The electron beam heated Nb source was outgassed and evaporated at about 25 Å/s for 30 min prior to each deposition sequence. Background pressure during evaporation was $3–4 \times 10^{-7}$ Torr (measured with no added argon).

A 3.0-cm beam diameter Kaufman ion source[4] was placed next to the electron-beam evaporator, such that the beam impinges on the substrate at an angle of 20° from normal. Argon gas was admitted through the ion source to a pressure of 5×10^{-5} Torr in the sample chamber. The ion energy is determined by the ion source anode voltage, and has an energy spread of less than 20 eV. The variation of ion flux across the substrate was maintained at less than 5% by adjusting the accelerator grid voltage.[4] No separate neutralizer was used.

Each sample was sputter cleaned immediately prior to coating, using 400-eV Ar^+ at 0.05 mA/cm^2 for 1 min, sufficient to remove about 50 Å. The sample was then covered with a shutter, the ion beam readjusted to the desired bombardment conditions, and the evaporator adjusted to the desired deposition rate. The time between sputter cleaning and deposition was 1–2 min. Samples were held to a copper plate by spring clips, and heated by a radiant heater to the desired temperature. The heat input from the ion beam, less than 0.01 W/cm^2, caused a temperature rise of less than 10 °C. For most of the data presented here, the film thickness was 2000 Å, deposited at 4 Å/s. In addition, superconducting NbN was formed by N_2^+ ion bombardment during evaporation of Nb (400 eV, 0.4 mA/cm^2, 4 Å/s, 30 °C).

C. Sample analysis

The film stress was calculated from the change in curvature of the substrate after deposition.[5] Separate measurements on adjacent samples agreed to within 2×10^9 dyn/cm^2. Thermal expansion mismatch is estimated to contribute no more than 2×10^9 dyn/cm^2 tensile stress. Film thickness was measured on each sample, both in a region bombarded by ions and a region shadowed from ions, to obtain the fraction of film resputtered during deposition. Room temperature resistivity and the resistive superconducting transition temperature were also measured with a

four-point technique. Concentrations of oxygen, argon, and carbon were measured in selected samples using electron microprobe and Rutherford backscattering.

III. RESULTS

Since substrate temperature strongly influenced the ion bombardment effects, the results are presented in two groups: samples coated at 400 °C, and samples coated at 30–200 °C. Additional results are then presented for other conditions.

A. Deposition temperature of 400 °C

The film stress is shown in Fig. 2(a) as a function of ion flux (100-eV and 400-eV Ar^+). In the absence of ion bombardment, the films have high tensile stress. Increasing ion flux changes the stress toward compressive, passing through zero stress in some samples. Curves A and B were measured on samples prepared in two runs under the same intended operating conditions. The difference is attributed to variations in residual gas incorporation, not measurement error.

The resistivity of samples from curves A, B and C, Fig. 2(a), is shown in Fig. 2(b) as a function of ion flux. Resistivity values are somewhat higher than the bulk Nb value of 14 $\mu\Omega$cm.[7–8] Transition temperatures (T_c) shown for curve A samples are near the bulk value of 9.3 K.[7–9] The electrical properties show little change with ion flux at 400 °C.

Atomic fractions of oxygen, argon, and carbon (by electron microprobe) in the samples of curve A, Fig. 2(a), are shown in Fig. 2(c) as a function of ion flux. Oxygen and carbon concentrations are difficult to determine accurately, due to the presence of surface oxides, background counts,

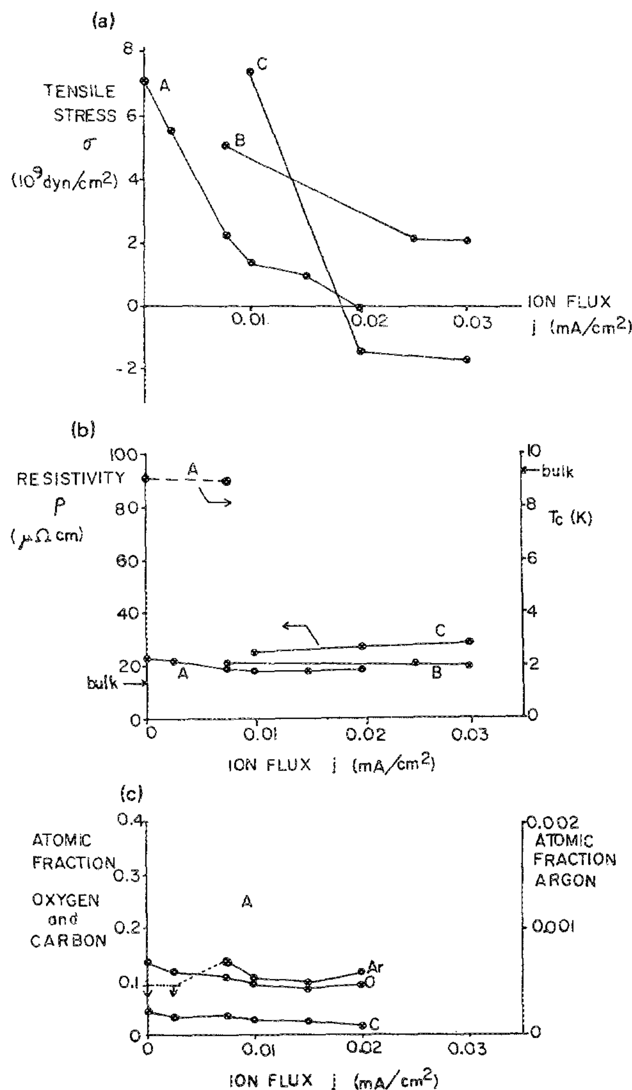

FIG. 2. (a) Stress vs ion flux for samples deposited at 400 °C, 4 Å/s. Curves A, B, 100-eV Ar^+. Curve C, 400-eV Ar^+. Film thickness 2000 Å. (b) Resistivity and superconducting transition temperature for samples from curves A, B, and C, Fig. 2(a). The bulk values for Nb are also shown. (c) Atomic fractions of oxygen, argon, and carbon in samples from curve A, Fig. 2(a), as measured by electron microprobe. Vertical arrows indicate Ar concentration was below the detectable limit of 0.05%.

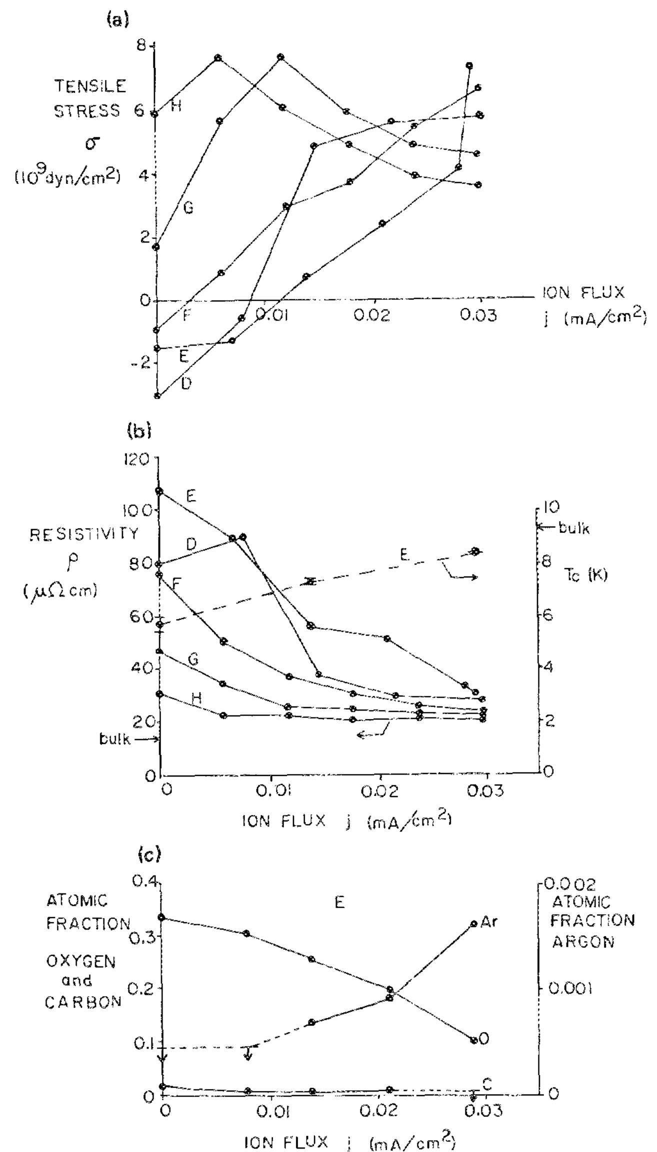

FIG. 3. (a) Stress vs ion flux for samples deposited below 200 °C at 4 Å/s. Curves D, E, at 30 to 100 °C. Curve F at 100 °C. Curve G at 150 °C. Curve H at 200 °C. Argon ion energy 100 eV, film thickness 2000 Å. (b) Resistivity and superconducting transition temperature for samples from curves D, E, F, G, and H, Fig. 3(a). Transition widths are indicated by vertical line lengths. Bulk values for Nb are also shown. (c) Atomic fractions of oxygen, argon, and carbon in samples from curve E, Fig. 3(a), as measured by electron microprobe. Vertical arrows indicate Ar and C concentrations below the detectable limits.

and surface carbon. These values should be regarded as upper limits on the concentration in the films. The oxygen and carbon content are slightly reduced by ion bombardment, and the argon content increases at the higher values of ion flux.

B. Deposition temperature of 30–200 °C

The dependence of stress on ion bombardment at sample temperatures below 100 °C has the opposite trend of the samples deposited at 400 °C. The stress vs ion flux (100-eV Ar^+) is shown in Fig. 3(a) for runs performed at 30–100 °C (curves D and E) and at 100 °C (curve F). At these temperatures, the stress is compressive in the absence of ion bombardment, and becomes tensile at values of about 0.01 mA/cm^2 ion flux, corresponding to an ion-to-atom arrival ratio of 0.03. At 150 °C [curve G, Fig. 3(a)] the stress starts tensile and passes through a peak with increasing ion flux. At 200 °C [curve H, Fig. 3(a)] the peak is shifted to lower values of flux.

The electrical properties show a strong influence of ion bombardment. The resistivity of samples from curves D, E, F, G, and H, Fig. 3(a), is plotted vs ion flux in Fig. 3(b), with T_c values from curve E. Both resistivity and T_c indicate improving film purity as a function of ion flux.

Electron microprobe results for samples of curve E, Fig. 3(a), are shown in Fig. 3(c). In contrast with the 400 °C samples, these room temperature samples show a strong decrease in oxygen and carbon content with increasing argon ion flux. Argon is also present at the level of 0.0015 atomic fraction (at 0.03 mA/cm^2), corresponding to an incorporated fraction of about 1.5% of the impinging ion flux. Rutherford backscattering analysis was also performed on the sample from curve E, Fig. 3(a), which received no ion bombardment. Oxygen was found at greater than 10 at. %.

C. Additional results

Some samples coated at room temperature showed tensile stress values on the order of 5×10^9 dyn/cm^2, and changed to compressive stress with increasing ion flux. These samples apparently incorporated less oxygen than those shown in Fig. 3.

The order of deposition in a given sequence also showed effects which we attribute to a gradual cleaning of the system during a run. Samples coated at the end of a sequence (at 150 °C, for example) had substantially higher tensile stress (up to 6×10^9 dyn/cm^2) than an equivalent sample coated at the start of a sequence. For consistency, all data shown in Fig. 2(a), 3(a) were obtained with a sequence of increasing ion flux during the run, except for curve D in Fig. 3(a). For that curve, the sequence of ion flux used was 0, 0.008, 0.03, 0.022, and 0.015 mA/cm^2.

Several experiments were carried out at higher ion energy and dose. Ion bombardment at 800 eV, 0.125 mA/cm^2, during deposition at 4 Å/s, 400 °C, caused a reduction in T_c of 0.5 K, from 8.1 to 7.6 K. An argon ion flux of 1.1 mA/cm^2 (at 10 Å/s) caused severe resputtering, a 20% increase in resistivity, and incorporated 7.4 at. % argon. Films of 1 μm thickness deposited under this level of bombardment had a frosty appearance.

The sample bombarded with N_2^+ ions during deposition had a resistive T_c extending from 14.5 to 9 K.

IV. DISCUSSION

The results demonstrate that Ar^+ ion bombardment at 100 eV can substantially modify Nb film stress. The dependence of stress on ion flux at 400 °C is from tensile to compressive, consistent with the trend reported by Hoffman and Gaerttner,[3] and Thornton and Hoffman.[2] The low values of flux needed to substantially change the stress (ion/atom ratios of several %) reflect the fact that intrinsic stress is a sensitive function of film microstructure. Using 100-eV Ar^+ ions at 0.01 mA/cm^2, which is typical of the range used in these experiments, the ion energy deposited per arriving Nb atom is about 3 eV/atom (at 4 Å/s). This energy is comparable to the activation energy for self-diffusion in Nb (4.2 eV),[11] and can therefore cause local rearrangement of the depositing film structure. The large effect on stress is therefore consistent with the picture outlined by Hirsch and Varga,[10] in which the critical dose needed to relieve intrinsic stress supplies to each atom the activation energy necessary for atomic rearrangement. It is advantageous to use low energy ions for this "annealing" process, since resputtering and ion implantation can be minimized. The sputtering yield of Nb with 100-eV Ar^+ is 0.1 atom/ion,[12] corresponding to only several % resputtering in the present range of flux. Also, incorporation of the ion species is almost absent at the conditions discussed here [Figs. 2(c) and 3(c)]. The large effects on stress cannot be attributed to ion implantation alone, since the change in stress due to the level of incorporated Ar is estimated at less than 10^9 dyn/cm^2, based on the values measured for oxygen incorporation. This conclusion has also been reached in other work.[3,10]

The results obtained at substrate temperatures below 200 °C emphasize the importance of residual gas incorporation in affecting stress. The effects of interstitial oxygen on T_c and resistivity in Nb are well documented.[8] T_c is suppressed at about 0.9 K per at. % oxygen, while resistivity increases at about 30 $\mu\Omega$cm per at. %.[8] The level of oxygen content necessary to cause the T_c and resistivity changes shown in Fig. 3(b) corresponds to about 3.6% in the samples deposited at room temperature without ion bombardment. Microprobe and backscattering analysis indicate higher levels, up to several tens %, which may be present in grain boundaries, or surface oxide. The cleaning effect by ion bombardment under these conditions is displayed in Fig. 3(b), and is analogous to the improvement in the quality of rf sputtered Nb under substrate bias.[9]

Using the analysis of resputtering applied to multicomponent alloy deposition,[13] we can calculate the sputter yield ratio of O to Nb which would account for the degree of cleaning due to ion bombardment in the samples of Fig. 3(b). An ion/atom ratio of 0.1 causes a decrease in resistivity from 100 to 30 $\mu\Omega$cm, corresponding to a reduction of interstitial oxygen from 3.6% to about 0.7%. The resputtered fraction at this value of ion flux (0.03 mA/cm^2) is about 0.1, which indicates a sputter yield ratio of O to Nb of about 50 (see Ref. 13, Fig. 3). If the larger values of O content indicated by microprobe analysis are used, the sputter yield ratio is esti-

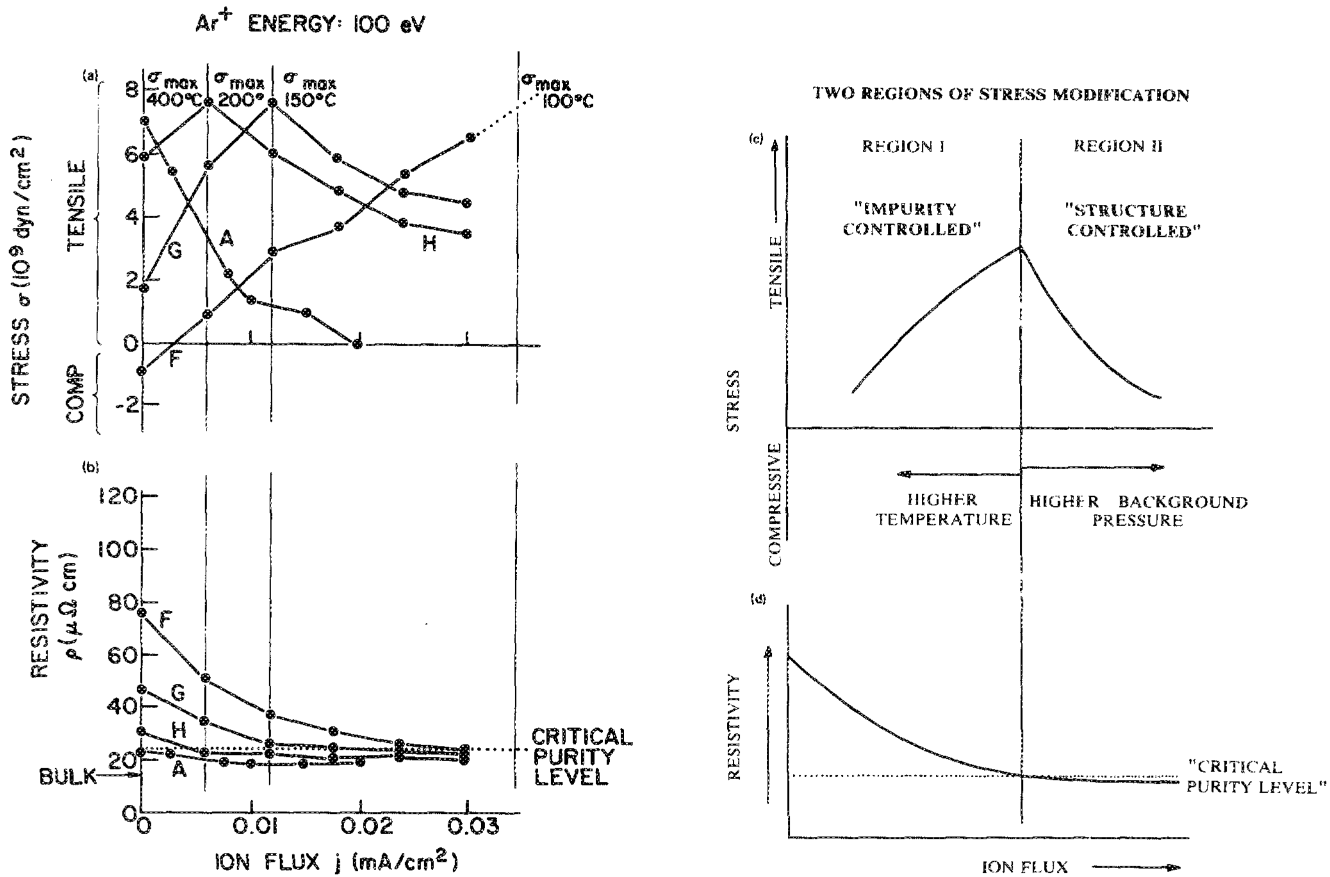

FIG. 4. (a) Stress vs ion flux for samples deposited at 4 Å/s. Curve A, 400 °C. Curve H, 200 °C. Curve G, 150 °C. Curve F, 100 °C. argon ion energy 100 eV, film thickness 2000 Å. (b) Resistivity vs ion flux, showing the correlation between the maximum in film stress and the critical purity level. (c) Schematic diagram showing impurity-controlled and structure-controlled regions of the stress vs ion flux curve. (d) Schematic diagram showing the correlation between the maximum in film stress and the critical purity level.

mated to be 40, indicating a sputter yield of oxygen of 4 atoms/ion, compared with the value of 0.1 for Nb. High sputter yield values of adsorbed gases have been reported in the literature,[14] and support the interpretation of a high degree of preferential sputtering caused by the low energy ion flux in the case of the room temperature samples.

The effect of this cleaning process on film stress seems to be accounted for by the decrease of oxygen content, but the trend toward compressive stress induced by momentum transfer does not occur in these oxygen-contaminated films. At intermediate temperatures [Curves G, H, Fig. 3(a)], however, the cleaning effect by ion bombardment seems to occur at low ion flux, until the resistivity is reduced to about 23 $\mu\Omega$cm. We interpret this region as impurity control of the stress. After this critical level of purity is reached, the trend toward compressive stress begins, resulting in a peak in tensile stress as a function of flux. We interpret this region where stress decreases with ion flux as structure control of the stress. In Figs. 4(a) and 4(b), some of the data is plotted to emphasize the correlation between the peak in the stress vs ion flux curve and the level of critical purity in the film. The peak in the stress curve occurs at lower values of ion flux for higher substrate temperatures due to the improved purity of the film at higher deposition temperatures. These results suggest that the momentum transfer process of "peening"[3] or "ion beam annealing,"[10] which we interpret as a structural modification, is operative only after the cleaning of the film is sufficiently complete. This qualitatively explains the trends shown in Fig. 3(a), and suggests that the atomic rearrangement process induced by momentum transfer in clean films may be inhibited in contaminated films, similar to the effects of impurities on grain growth.[15] These concepts are shown schematically in Figs. 4(c) and 4(d), in which the regions of "impurity controlled" and "structure controlled" stress modification are defined on the curve of stress vs ion flux. The boundary between these two regions occurs where the film purity reaches the "critical purity level." This boundary, and hence the peak of tensile stress, moves to lower values of ion flux with increased substrate temperature, and moves to higher values of ion flux with higher background pressure.

This picture is further supported in some of the published data on film stress in magnetron sputtering. The data in these papers shows the stress passing over a maximum tensile value and decreasing as a function of gas pressure,[2,16] with resistivity values saturating near bulk values at the pressure corresponding to the maximum in stress. We believe this decrease in resistivity to a value approaching the bulk value represents a cleaning of the film due to the more energetic substrate bombardment at lower pressures.

The results presented in this paper point to a combination of effects of ion bombardment during the deposition of reac-

tive metals. The details of these effects on microstructure and stress are starting to be revealed using ion beam techniques. Although the results are strongly influenced by background gas pressure, future work using ion beams should be able to distinguish between the possible mechanisms of ion impact which influence stress. In addition, the demonstration with N_2^+ ion bombardment of a T_c near the bulk value of 16 K for NbN[17] shows the utility of ion bombardment during evaporation in forming reactive compounds.

ACKNOWLEDGMENTS

We thank A. Segmuller for help with x-ray measurements, J. L. Speidell for substrate preparation, J. M. Viggiano for T_c measurements, J. D. Kuptsis, R. J. Savoy, and A. T. Boulding for electron microprobe measurements, and J. P. Ottaviani and P. Saunders for Rutherford backscattering measurements.

[1]R. W. Hoffman, in *Physics of Nonmetallic Thin Films*, edited by C. H. S. Dupuy and A. Cachard (Plenum, New York, 1976), p. 273.
[2]J. A. Thornton and D. W. Hoffman, J. Vac. Sci. Technol. **14**, 164 (1977); J. A. Thornton and D. W. Hoffman, J. Vac. Sci. Technol. **18**, 203 (1981); D. W. Hoffman and J. A. Thornton, Thin Solid Films **45**, 387 (1977).
[3]D. W. Hoffman and M. R. Gaerttner, J. Vac. Sci. Technol. **17**, 425 (1980).
[4]H. R. Kaufman, J. Vac. Sci. Technol. **15**, 272 (1978).
[5]A. Segmuller, J. Angilello, and S. J. LaPlaca, J. App. Phys. **15**, 6224 (1980).
[6]P. V. Plunkett, R. M. Johnson, and C. D. Wiseman, Thin Solid Films **64**, 121 (1979).
[7]Y. Saito and T. Anayama, J. Low Temp. Phys. **21**, 169 (1975).
[8]C. C. Koch, J. O. Scarbrough, and D. M. Kroeger, Phys. Rev. B **9**, 888 (1974); W. DeSorbo, Phys. Rev. **132**, 107 (1963).
[9]A. F. Mayadas, R. B. Laibowitz, and J. J. Cuomo, J. Appl. Phys. **43**, 1287 (1972).
[10]E. H. Hirsch and I. K. Varga, Thin Solid Films **69**, 99 (1980).
[11]N. L. Peterson, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 22, p. 409.
[12]G. K. Wehner, Report No. 2309, General Mills, Minneapolis (1962).
[13]J. M. E. Harper and R. J. Gambino, J. Vac. Sci. Technol. **16**, 1901 (1979).
[14]H. F. Winters and P. Sigmund, J. Appl. Phys. **45**, 4760 (1974).
[15]H. Caswell, J. Appl. Phys. **32**, 2641 (1961); J. B. Preece, H. Wilman, and C. P. H. Stoddart, Phil. Mag. **16**, 447 (1967).
[16]C. T. Wu, Thin Solid Films **64**, 103 (1979).
[17]B. W. Roberts, NBS Tech. Note 408 (1966).