THE EFFECT OF LOW ENERGY ION BOMBARDMENT ON THE CRYSTALLOGRAPHIC ORIENTATION OF THIN FILMS

by

LOCK SEE YU

S.B. Massachusetts Institute of Technology (1984)

Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements of the Degree of

MASTER OF SCIENCE IN MATERIALS SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 1985

© Lock See Yu 1985

The author hereby grants to M.I.T. permission to reproduce and to distribute copies of this thesis document in whole or in part.

Signature of Author

Department of Materials Science and Engineering

August 9, 1985

Certified by

L. Rafael Reif, Thesis Supervisor

Certified by

James M.E. Harper, IBM Research Supervisor

Accepted by

Bernhardt J. Wuensch, Chairman, Departmental Graduate Committee

OCT 21 1985
THE EFFECT OF LOW ENERGY ION BOMBARDMENT ON
THE CRYSTALLOGRAPHIC ORIENTATION OF THIN FILMS

by

LOCK SEE YU

Submitted to the Department of
Materials Science and Engineering
in Partial Fulfillment of the Requirements of the
Degree of Master of Science in Materials Science
on
August 9, 1985

ABSTRACT

The effect of simultaneous low energy ion bombardment during the deposition of thin films is investigated. The films were prepared by ion beam sputter deposition onto amorphous fused silica substrates. Direct bombardment of the growing film occurred at an incident angle of 20° to the surface of the substrate using Ar ions of 200 eV energy.

Ion bombardment has been found to directly influence the crystallographic orientation of the resultant film. X-ray diffraction and transmission electron microscopy reveals that ion bombarded films possess a texture or preferred orientation, with the degree of ordering increasing with increasing ion current density. The direction of ion impact is observed to be an important parameter in the preferred orientation or restricted fiber texturing of the film.

Increased adatom surface mobility due to ion bombardment, the occurrence of low energy ion channelling, and the dependence of sputter yield on orientation are discussed as factors contributing to the observed effects.

The material studied most extensively is Nb. Cu and Al were also studied, but no strong evidence of bombardment induced orientation effects were observed.

Thesis Supervisor: Dr. L. Rafael Reif

Title: Associate Professor of Electrical Engineering
# CONTENTS

List of Figures ................................................. 4  
List of Tables .................................................. 6  
Acknowledgements ............................................. 7  
Introduction .................................................. 8  
Fundamental Effects of Ion Surface Interactions ............ 11  
Property Modifications due to Ion Bombardment .......... 15  
Principles of Ion Source Operation ......................... 21  

### Experimental Procedure ...................................
  A. Experimental Apparatus ................................. 29    
  1. Pumping System ......................................... 30    
  2. Substrate Holder Assembly ............................. 31    
  3. Ion Sources, Current Probe, and Target ............. 32
  B. Experimental Conditions ............................... 34    
  1. Vacuum .................................................. 34    
  2. Target Ion Source ...................................... 34    
  3. Target .................................................. 35    
  4. Substrate Ion Source ................................... 36    
  5. Substrates ............................................. 38

### Methods of Analysis ......................................
  A. Pole Figure Method of X-ray Analysis ............... 46
  B. Transmission Electron Diffraction .................... 51

Results ......................................................... 60
  A. Pole Figure Results .................................... 60    
  1. Films Without Simultaneous Ion Bombardment ....... 60    
  2. Films With Ion Bombardment During Deposition .... 61    
  3. Other Pole Figure Results ............................ 63
  B. Transmission Electron Diffraction Results .......... 64

Discussion ..................................................... 82
Conclusion .................................................... 88
Suggestions for Future Studies ............................. 90
References ..................................................... 92
LIST OF FIGURES

Figure 1. Ion beam source schematic.......................26
Figure 2. Schematic of extraction grid region..............27
Figure 3. Electrical potentials in an ion
beam system........................................28
Figure 4. Schematic of experimental set-up...............39
Figure 5. Schematic of ion probe configuration............40
Figure 6. Current density as a function of
discharge current..................................41
Figure 7. {100} poles of a cubic crystal.................55
Figure 8. The stereographic projection....................55
Figure 9. Schematic of slits and goniometer
head for Schulz's reflection method.................56
Figure 10. Ray diagrams for electron microscope.........57
Figure 11. Pole figure for Nb without simult-
aneous ion bombardment............................66
Figure 12. Pole figure for Nb at j=0.20mA/cm²..............67
Figure 13. Pole figure for Nb at j=0.30mA/cm².............68
Figure 14. Pole figure for Nb at j=0.35mA/cm².............69
Figure 15. Pole figure for Nb at j=0.45mA/cm².............70
Figure 16. Pole figure for Nb at j=0.55mA/cm².............71
Figure 17. Pole figure for Nb at j=0.60mA/cm².............72
Figure 18. Pole figure for Nb at j=0.65mA/cm².............73
Figure 19. Degree of orientation as a function
of current density at substrate....................74
Figure 20. Ion/atom arrival rate ratio as a
function of current density.........................75
Figure 21. Fraction of material respattered as
a function of current density.....................76
Figure 22. Pole figure for Nb bombarded after
deposition at j=0.55mA/cm².......................77
Figure 23. Pole figure for Nb with only the first 300 - 500Å subject to ion bombardment ......................... 78

Figure 24. Pole figure for Nb with ion bombardment during first half of deposition time .................. 79

Figure 25. Diffraction patterns from Nb with electron beam at normal incidence ............... 80

Figure 26. Diffraction patterns from Nb with sample tilted at -40°, +40° ...................... 81

Figure 27. Standard 110 projection ......................... 87
LIST OF TABLES

Table 1. Fixed target ion beam parameters.............42
Table 2. Variable target ion beam
parameters..............................42
Table 3. Sputtering rates and arrival
fluxes..................................43
Table 4. Fixed substrate ion beam
parameters...............................44
Table 5. Variable substrate ion beam
parameters...............................44
Table 6. Diffraction rings for bcc
textured material.........................58
Table 7. Diffraction rings for fcc
textured material.........................59
ACKNOWLEDGEMENTS

I wish to express my deepest gratitude to all the members of the IBM C.S.S. Materials Laboratory for their unrelenting support, assistance, and friendship. I am especially grateful to J.M.E. Harper for his guidance throughout this project, and D.A. Smith for his transmission electron microscopy and invaluable discussions. I would also like to thank J.J. Cuomo for providing me with the opportunity to work in his laboratory, and L.R. Reif for helpful comments and discussions.

Most importantly, I want to thank C.V. Jahnes for being wonderful.
INTRODUCTION

Energetic particle bombardment during film formation can strongly influence the chemical, physical, and structural properties of the resultant film. The observed effects are attributed to the ion-surface interactions that occur when ions bombard the surface of a growing film. These effects are directly dependent on the ion parameters, such as ion energy, flux, and mass, as well as on the substrate parameters, such as material, temperature, and orientation.

Various methods are available for achieving ion bombardment during film growth. In bias sputtering, an applied negative bias to the substrate electrode, or anode, will alter the electric field near the anode causing a flux of energetic ions to the substrate. (1) Similarly, an applied substrate bias in magnetron sputtering (2), triode sputtering (3), and ion plating (4) will lead to substrate ion bombardment. Plasma enhanced chemical vapor deposition (PECVD) uses a radio frequency plasma to generate reactive species such as ions, radicals, excited species, and metastables. (5) Substrates immersed in the plasma region are subject to ion and energetic neutral
bombardment. In ionized cluster beam deposition (ICBD),
films are formed from singly ionized macroaggregates of
500 - 2000 loosely coupled atoms. (6) The ionized clusters
are propelled towards the substrate by a high negative
potential to the substrate holder.

Ion beam processing offers the highest degree of
control compared to the other plasma processes. Ion flux,
ion energy, and direction of ion impact can all be indepen-
dently controlled. The Kaufman ion source, originally
designed as an ion thruster for space propulsion (7), is
the most widely used broad beam ion source today. Films
can be bombarded during vapor phase condensation, e.g.
electron beam evaporation, or during simultaneous ion beam
sputter deposition.

In the low energy range (25 - 1000 eV), ion bombard-
ment can significantly influence the kinetics of film
formation, including surface reaction kinetics, nucleation
and growth kinetics, sticking probabilities, and interface
interdiffusion rates. (8,9) Property modifications caused
by irradiation include enhancement of substrate-film
adherence (10), intrinsic stress modification (10,11),
lowering of the critical temperature for epitaxial film
growth (8), increasing the degree of preferred orient-
ation (12) and changes in crystal orientation. (13,14)

The fundamental effects resulting from irradiation during film growth, and which underlie thin film property modification, include an increase in adatom mobility or surface migration, the displacement of surface atoms, the desorption of adsorbed impurities, sputtering, and trapping of incident ions on the substrate surface.

In this thesis, the effects of low energy ion bombardment on the crystallographic orientation of niobium is studied. A dual ion beam system is used, enabling independent control of the parameters of both beams. A primary ion beam is used to sputter the target to provide a flux of atoms arriving at the substrate, while a secondary or substrate ion beam provides direct ion bombardment of the substrate surface. Changes in the degree of preferred orientation in the films are observed as a function of ion current density. The films are analyzed by both x-ray and electron diffraction methods. The results will be discussed in terms of effects caused by ion-surface interactions.
FUNDAMENTAL EFFECTS OF ION-SURFACE INTERACTIONS

Property modification caused by ion bombardment during film formation can be discussed in terms of the first-order effects of ion bombardment or what fundamentally occurs when energetic ions impact on a solid surface. Some of the phenomena that have been observed include an enhancement of adatom surface mobility, the physical displacement of surface atoms, the desorption of adsorbed impurities, sputtering, and shallow ion implantation or trapping of incident ions on the substrate surface. (9)

An increase in surface migration due to ion bombardment has been reported by many investigators. (1,10,12,15,17) Dranova and Mikhailovski (15) conducted a study of tungsten crystals using field-ion microscopy and observed that helium ion bombardment at energies of 500 - 2500 eV resulted in the creation of small protuberances on the tungsten tip. They concluded that surface migration activated by ion bombardment was responsible for these occurrences. Marinov (12) found that with simultaneous substrate bombardment silver crystallites appeared on areas of a substrate completely shielded from silver deposition, although in the absence of bombardment a sharp edge separated the shuttered and
unshuttered regions.

The physical displacement of surface atoms due to momentum transport by the ion flux is another fundamental effect of irradiation during film growth. Cavaille and Drechsler (16) observed that when the angle of ion incidence deviates from normal to the substrate surface, "tails" appear which signify displaced surface atoms and indicate the angle and direction of ion impact. They calculate the number of surface atoms transported to be proportional to the flux of ions to the surface. Although these investigators refer to this effect as "experimental proof for the existence of an ion impact induced surface diffusion," it is important to distinguish between physical displacement due to momentum transfer, which has a directional component, from the energetics of diffusion, which is non-directional and depends on compositional gradients.

At kinetic energies greater than a few eV, ion bombardment can effectively remove impurities or contaminants from the surface. The adsorption energy is approximately 0.1 - 0.5 eV for physically adsorbed atoms on the substrate surface, and approximately 1 - 10 eV for chemically adsorbed atoms. (6) Therefore, at kinetic energies
slightly above the impurity adsorption energy, ions can effectively clean the substrate surface.

The threshold energy for sputtering by rare gas bombardment can be approximated by $4H$, where $H$ is the enthalpy of sublimation of the target. (17) For most solids this corresponds to energies of 20 – 40 eV. (18) Bombardment energies for etching of thin films typically range from 100 – 1000 eV resulting in sputtering yields of 0.1 – 10 atoms removed per incident ion. (8) For low energy/light ion sputtering Matsunami et al. (19) propose the following empirical formulation for the energy dependence of the sputtering yield at normal incidence sputtering:

$$S(E_i) = \frac{0.42}{U} a(m_t/m_i) \left[1 - \frac{E_{\text{th}}}{E_i}\right]^{0.5} \sigma_n(E_i, Z_i, Z_t)$$

where $U$ is the binding energy of the target, $a(m_t/m_i)$ is a factor describing the efficiency of momentum transfer for elastic collisions, $E_{\text{th}}$ and $E_i$ are the sputtering threshold and incident ion energies, respectively, and $\sigma_n$ is the cross section for nuclear stopping, which is dependent on the ion energy and $Z_i$ and $Z_t$, the atomic numbers of the ion and target, respectively. This relation is in
agreement with their experimental results down to values of \( E_i/E_{\text{th}} = 1.1 \). However, at ion energies lower than the threshold energy this equation is mathematically invalid.

An incident ion can be trapped or implanted in a growing film. The probability that an ion will be trapped is a function of its incident energy and mass. Rare gas atoms are only weakly physisorbed with binding energies of about 0.2 eV. These atoms are almost immediately desorbed, with an average residence time of less than \( 10^{-9} \) seconds at room temperature. For energetic species, the threshold energy for trapping, \( E_T \), ranges from tens of eV for light particles to hundreds of eV for heavy particles. Anderson and Sigmund (20) suggest that \( E_T \) can be estimated using a generalized Born-Mayer potential:

\[
E_T = 10^{-15} N_s \text{(atoms/cm}^2\text{)} (Z_i Z_t)^{0.75}
\]

where \( Z_i \) and \( Z_t \) are the atomic numbers of the ion and target, respectively, and \( N_s \) is the surface density of target atoms. For argon ion bombardment of a niobium surface, \( E_T \) is approximately 200 eV.
PROPERTY MODIFICATIONS DUE TO ION BOMBARDMENT

The fundamental effects of ion-surface interactions mentioned above can lead to significant property changes in the resultant film. The range of ion energies at which property modifications occur can vary substantially, from tens of eV to lower the critical temperature for epitaxial film growth to tens of keV to cause orientation changes in crystalline films. Some of the more significant phenomena caused by ion bombardment during film growth include an enhancement of substrate-film adherence (10,21), intrinsic stress modification (10,11), a change in the orientation of crystalline films (13,22,23,24), a reduction of the critical temperature for epitaxial film growth (14,25,26), and an increased degree of preferred orientation (12). These effects can influence the nucleation and growth kinetics of film formation.

The improvement in film adhesion resulting from ion bombardment during deposition can be attributed to two effects. In the high energy range, where incident energies are tens of keV, adhesion is improved by ion beam mixing of the film and substrate materials at the interface. (21) However, this "brute force" interface interdiffusion method
can lead to significant damage well below the interface due to implantation of the high energy ions. In the lower energy regime (65 - 3000 eV), Hirsch and Varga (10) found that bombardment improved substrate adherence by causing a strengthening of the interfacial bond through the formation of a transition layer consisting of a mixture of substrate and film materials, not unlike the high energy case. However, they also noticed a reduction in the intrinsic film stress when the ion current density exceeded a critical minimum value. Their observations indicate an annealing effect caused by bombardment induced temperature spikes. From the relationship between electrical energy and thermodynamic temperature, \( E(eV) = 1.5kT \), extremely high thermal energies can result from ion energies of only a few eV. Takagi (9) asserts that effects similar to those produced by substrate heating can be expected by using energetic ion beams. Further work by Cuomo et al. (11) on stress modification of niobium films through ion bombardment during film growth is in agreement with the study by Hirsch and Varga. They also point out that the cleaning effect of ion bombardment aids in the annealing process. They found that the atomic rearrangement that occurs during annealing is inhibited in niobium films contaminated with oxygen, with stress modification delayed until a sufficiently pure film is exposed.
A lowering of the critical temperature for epitaxial film growth has been observed for films subject to ion bombardment during deposition. Babaev, Bykov, and Guseva (14) report a 35% drop in the epitaxial temperature of antimony films deposited onto a sodium chloride substrate, from 230°C without bombardment to 150°C with bombardment by 400 eV argon ions. Ota (26) has achieved epitaxial growth of copper films on alkali halide substrates at 140°C with simultaneous 400 eV copper ion bombardment, although a substrate temperature of 180 - 190°C was necessary for epitaxial growth without irradiation. Ota's study suggests an exponential relationship between the ion intensity, $P_i$, and reciprocal epitaxial temperature, $T_e^{-1}(°K^{-1})$, where $P_i$ is the product of the ion accelerating voltage and the ion current density. A threshold energy of 50 eV was necessary to form epitaxial copper films. Of particular relevance to silicon on insulator (SOI) technology is the epitaxial growth of silicon on sapphire. Narusawa et al. (25) report a 150°C decrease in the epitaxial temperature of (100)-silicon on (1102)-sapphire substrates when bombarded with a partially ionized silicon vapour. An ion accelerating voltage of 200 V and a 1% ionization efficiency produced the epitaxial temperature drop from 575°C without bombardment to 425°C with bombardment.
Babaev et al. (14) explain the observed epitaxial temperature reductions in terms of ion irradiation controlled nucleation and growth kinetics. In the critical stage of film formation ion irradiation leads to an increase in the nucleation rate, and thus a finer film structure. The increase in the concentration of smaller nuclei causes the development of nucleus orientation, which is enhanced by substrate orientation action. The growth kinetics after nucleation are determined by the increase in the mobility of surface atoms under irradiation.

Related to the occurrence of irradiation induced reduction in epitaxial temperatures is the increase in the degree of preferred orientation in ion bombarded films. Marinov's (12) study of the influence of ion bombardment on the initial stages of silver film formation shows that a preferred crystal orientation arises at the onset of the crystallization process when simultaneously ion bombarded, although without bombardment the islands were randomly oriented. He notes the marked influence that ion bombardment has on the kinetics of film formation where the enhanced mobility of adatoms subjected to low energy ion bombardment leads to the preferred crystal orientation.

A total change in the crystal orientation of a film
subject to ion bombardment has been reported by a number of investigators. (13,22,23,24) Smith and van Wyk (22) conducted a study using high energy (40 keV) copper ions to bombard a pre-deposited copper target. Prior to bombardment the copper target was found to have a \{111\} preferred orientation, where a large fraction of the crystallites were oriented with the \{111\} planes parallel to the substrate surface. By comparing the intensities for the 111, 200, and 220 x-ray diffraction peaks for bombarded and unbombarded samples they noticed a 49-fold increase in the 220 reflection. This indicates a preponderance of \{110\} planes parallel to the substrate surface resulting from ion bombardment. Dobrev (13) noticed the same orientation change in silver films bombarded with 10 keV argon ions. However, the heating of the silver films up to 500°C, (greater than half the melting temperature), could not produce the same orientation change. Marinov and Dobrev (23) found that cadmium films, regardless of their initial orientation, show a \langle11\bar{2}0\rangle orientation after bombardment. These investigators point out that ion irradiation results in films oriented so that there is a minimum energy loss per unit distance of the incident ion. In other words, ion bombardment reorients the crystallites to a configuration where the channelling direction of the material is aligned with the direction of the ion beam.
Smith and van Wyk (24) also note that the sputtering yield of polycrystalline materials is dependent on crystal orientation. Orientations having high sputter yields tend to be unfavourable channelling orientations. Likewise, channeling orientations have lower sputter yields due to the higher probability that an incident ion will be lost to channelling and therefore not contribute to sputtering.

Other cases of ion bombardment induced property modifications are the formation of hard diamondlike carbon films (27,28), and an increase in the refractive index of zirconium dioxide films due to an increase in the packing density of the films (29).
PRINCIPLES OF ION SOURCE OPERATION

An ion beam system is composed of three sections: a plasma source which generates the ions, the extraction/acceleration grids which extract the ions from the plasma source and propels them toward a target, and a target or substrate. Figure 1 shows a schematic of the Kaufman ion source, which is most commonly used today.

There are three requirements for maintaining a glow discharge in the ion source:

1. sufficient gas in the discharge chamber
2. a source of electrons (cathode)
3. an accelerating voltage for the electrons ($V_d$)

A tungsten or tantalum filament acts as a cathode and thermionically emits electrons, which are accelerated by a potential difference, $V_d$, between the cathode and anode. $V_d$ is called the discharge voltage and must be greater than the ionization potential of the gas (15.8 eV for argon). The discharge voltage is usually operated at about 40 - 60 V to maintain a glow discharge. To sustain a plasma in the ion source the amount of gas bled into the chamber will
cause a pressure increase to the $10^{-4}$ Torr range. Ionization efficiency is improved by applying a magnetic field to the discharge area so that electrons cannot pass directly from the cathode to the anode but must follow a helical path and suffer more collisions enroute.

The discharge plasma establishes itself between the anode, cathode, chamber walls, and screen grid. The plasma potential is typically a few volts positive of the anode and is determined by the rate of loss of electrons and ions from the plasma. The screen grid and chamber walls are held at cathode potential, creating a cathode sheath at these surfaces. Electrons are accelerated across the sheath by the potential difference $V_d$ and bombard gas atoms to produce ions and secondary electrons. The ions are also accelerated by the potential difference $V_d$. Therefore, to minimize sputtering in the ion source, $V_d$ is kept no higher than necessary to sustain a stable discharge.

The extraction region consists of a set of grids with perfectly aligned arrays of holes. The extraction grid geometry limits the maximum ion current density that can be extracted into a beam, making the extraction grid region the most critical component of the ion source. Figure 2 is a schematic of the extraction grid region.
In extracting an ion beam from the discharge plasma the anode is raised to a positive voltage with respect to ground. This raises the cathode, chamber walls, and screen grid to the anode potential less the discharge voltage. The plasma potential is determined by the anode voltage, but is a few volts positive of it due to the higher electron velocities relative to the ion velocities. The energy of the extracted ions is approximately 5 V above the anode voltage. A diagram of the electrical potentials in an ion beam system, with a discharge voltage of 50 V and an anode voltage of 1800 V, is shown in Figure 3.

The outer or accelerator grid is biased negatively with respect to ground, typically ranging from -100 to -300 V. The accelerator grid serves a dual purpose. The negative voltage applied to the grid accelerates the ions through the extraction region. For example, an anode voltage of 1800 V and an accelerator voltage of -100 V will accelerate the ions by a $1800 - (-100) = 1900$ V potential difference. The ions, upon entering the beam plasma, will decelerate to 1800 eV. The accelerator grid also acts as a shield to prevent electrons from back-streaming into the positive discharge area.

A main concern in operating ion sources is to maximize
the ion current density at a given ion energy, therefore minimizing process time. However, the maximum ion current density extractable from the plasma is space charge limited, with the maximum ion flux given by Child's Law:

\[
 j_{\text{max}} = \frac{(4 \varepsilon_o/9)(2e/m)^{0.5} V_t^{1.5}}{\Delta^2}
\]

where \( j_{\text{max}} \) is the maximum current density, \( V_t \) is the total potential difference between the grids, \( \varepsilon_o \) is the permittivity of space, \( e/m \) is the charge to mass ratio of the ion, and \( \Delta \) is the separation between the grids as shown in Figure 2. The ceiling on the ion flux is determined by the fixed spacing between the grids, and severely restricts many applications which require a low ion energy to minimize substrate damage. Harper et al. (30) have found that by converting to a single extraction grid of very fine aperture size the problem of limited ion flux is circumvented. Current densities of over 1.0 mA/cm\(^2\) can be achieved below 100 eV ion energy.

For insulating targets a neutralizer, or source of electrons, is necessary to prevent any surface charging effects caused by the positive ion beam. The simplest neutralizer configuration is a thermionically emitting hot
filament immersed in the beam.
FIGURE 1. Ion beam source schematic.
FIGURE 2. Schematic of extraction grid region.
FIGURE 3. Electrical potentials in an ion beam system. (Not drawn to scale.)
EXPERIMENTAL PROCEDURE

A. Experimental Apparatus

All experiments described herein are performed in a single vacuum system to avoid any unnecessary inconsistencies. Unless otherwise stated, all vacuum seals are made with Viton o-ring gaskets.

The experimental chamber is a stainless steel cylinder, with a diameter of 19.5in and a height of 10in. An 8in circular viewport, or window, in the chamber allows visual access to the experiments in progress. The window is made of Pyrex, with a diameter of 9.125in and a thickness of 0.625in. The window will serve as reference for the "front" of the system.

At 90° to the right of front is a 10in flange mounted onto the chamber. This flange holds the feedthroughs for the substrate holder and heater as well as the electrical wiring feedthroughs for the heater, the substrate shutter feedthrough, and the feedthrough for the ion current probe. At 90° to the left of the window is another 10in flange. This flange holds the electrical and gas feedthroughs for
the substrate ion source. Also on this flange is a small window, 2in in diameter, which allows direct sight of the substrate platform. Diametrically opposite the front window is the high vacuum gate valve, which separates the vacuum chamber from the pumping system. The top and bottom lids of the vacuum chamber are made of aluminum. The top plate supports the target ion source and its electrical and gas feedthroughs. The bottom plate supports the target and the water cooling lines to the target, as well as the ion current probe electrical feedthroughs.

1. Pumping System

Vacuum is attained via a rotary-vane mechanical pump and a turbo pump, both manufactured by Balzers. The turbo pump can achieve a maximum pumping speed of 500 liters per second. In addition to these pumps is a titanium sublimation pump. This pump is placed in the "stack" area directly preceding the turbo pump. The resistive heating of a titanium filament produces sublimation of highly reactive titanium atoms, which act as very effective getters of oxygen and water vapor, as well as other residual gases. A liquid nitrogen cooled shroud surrounding the sublimation pump promotes condensation of the gettered product onto the shroud lining. This pump can be easily
removed for filament replacement, and is sealed to vacuum with a copper gasket. The chamber walls are heated every evening with resistive heater tape to outgas adsorbed residual gas molecules.

2. Substrate Holder Assembly

The substrate holder assembly consists of a substrate platform and a radiant heater, both attached to a rotatable shaft. Figure 4 is a schematic of the experimental area. The shaft is lined with a water jacket to allow cooling water to reach the cooling stage below the heater. For experiments that do not require substrate heating the radiant heater is removed to allow direct contact between the substrate platform and cooling stage. The substrate platform is made of solid copper of 6in diameter and approximately 0.25in thickness. On the surface of the platform are shallow recesses machined into the copper to assure that from run to run the substrates are always sitting on the same spot. Due to the small diameter of the substrate ion beam, only one 1in diameter substrate is used per experiment. The necessity for adequate shielding of substrates not involved in an experiment precludes the mounting of more than two substrates on the platform per pumpdown. For experiments conducted at elevated temperatures the heater
provides radiant heating of the platform from three quartz-iodine lamps. Painstaking care is taken to accurately position each substrate in order that references, such as direction of incidence of the substrate beam or the point closest to the top plate of the chamber, can be readily identified. A small clip positioned 90° to the direction of bombardment and pointing towards the top plate allows easy identification of the position of the substrate during an experiment. Additional markings on the substrate holder shaft allow reproducible external positioning of the substrate platform.

The substrate shutter is mounted onto a rotatable shaft that can be easily swung into a position where both substrates are completely shielded from deposition and/or ion flux, e.g. during target conditioning, or to a position where an experiment can be performed on one substrate while the other is completely protected. The shutter is positioned less than 0.25in away from the substrate platform.

3. Ion Sources, Current Probe, and Target

As shown in Figure 4, the experimental system contains two ion sources. The target source, manufactured by Ion Tech, has a grid diameter of 2.5cm and is water cooled. The substrate ion source has 3.0cm diameter grids and is
made by IBM for internal use. This source is not water cooled. The grids for both sources are made of graphite. Both the target and substrate ion sources are operated from Advanced Energy/Ion Tech power supplies, model ID-3500.

The target ion source sputters a 6in diameter target, inclined towards the substrates, to provide a flux of material to be deposited. The target is water cooled, and is bolted to the bottom plate so that its location is consistent for all the experiments.

An ion current probe is used to measure the flux of ions from the substrate source. The probe is mounted onto a rotatable feedthrough attached to the 10in flange to the right of the system. A schematic of the ion probe is shown in Figure 5. The probe is biased to about -15 V to repel the low energy electrons in the beam. The current collecting portion of the probe has a surface area of 1cm². Since the current density from the target source is not critical to the experiments, no probe is used to measure its flux.

During ion current measurement the probe is positioned directly in front of the substrate ion source, but is otherwise swung away from the substrate area. From time to time
during an experiment the probe is quickly swung into position to check the current density of the beam so that any current drift can be corrected.

B. Experimental Conditions

1. Vacuum

A base pressure of less than $2 \times 10^{-7}$ Torr is attained for each pumpdown. Due to the highly reactive nature of niobium, the titanium sublimation pump is operating for the duration of each experiment. The chamber pressure is increased to $2 \times 10^{-4}$ Torr of argon for each experiment, with an equal pressure of $1 \times 10^{-4}$ Torr contributed by each ion source.

2. Target Ion Source

The target ion source is water cooled at all times during its operation, and produces a beam of argon ions. The target beam parameters are kept as consistent as possible from run to run. The fixed parameters of the target beam are listed in Table 1, and variable beam parameters are listed in Table 2. It should be noted that these
variable parameters are determined by the values used for the fixed parameters. A fixed discharge voltage of 50 V will set the discharge current which, for these experiments, will range anywhere from 0.60 - 0.75 A. The current-voltage relationship for the accelerator grid is consistently at 2 mA current for an applied voltage of -200 V. The cathode current is adjusted so that the beam current is constantly at a value of 40 mA. Due to the constant erosion of the cathode filament, resulting from ion bombardment in the discharge area, the cathode current can range anywhere from 5.5 A for a newly installed filament to 3.5 A for a worn filament.

3. Target

The target materials used for these experiments are niobium, aluminum, and copper. The distance from the target ion source to the target is approximately 4 in, with the target inclined towards the substrate platform at an angle of 37° to the bottom plate surface. The target is a solid disk of material, 6 in in diameter and about 0.25 in thick, water cooled from the bottom.

The sputter deposition rates for the three materials by 1800 eV argon ions are listed in Table 3. The
arrival flux of depositing atoms can be calculated from the following relationship:

\[
\text{flux} = \text{(rate)} \cdot \text{(density)} \cdot (6.02 \times 10^{23}) \cdot (10^{-8}) / \text{(weight)}
\]

\[
\frac{\text{atoms}}{\text{cm}^2 \text{sec}} = \frac{\text{Å/sec}}{(g/cm^3)} \cdot \frac{(\text{atoms/mole})}{(cm/Å)} / (g/mole)
\]

The target is preconditioned by presputtering for 20 - 30 minutes before deposition if it has been exposed to atmosphere.

4. Substrate Ion Source

The substrate ion source is also operated using an argon gas flow. The source is positioned so that the center of the ion beam is level with the center of the substrate. The substrate source is inclined at a glancing angle of 20° to the surface of the substrate. The distance between the source and the substrate is about 2in. The fixed and variable parameters of the substrate ion beam are listed in Tables 4 and 5, respectively.

Again, the accelerator current is determined by the voltage applied to the accelerator grid. The beam current density determines the values for all the remaining variables. The substrate ion beam current density is critical
to the experiment. Therefore, an open probe, discussed in a previous section, is used to monitor the ion flux to the substrate.

An important consideration regarding an ion beam is its divergence. Beam divergence can result from a number of causes, e.g. misaligned grids, or inappropriate accelerator voltage. Divergence of the ion beam can lead to false current density readings, especially if measurements are not taken at the substrate. However, geometrical and mechanical reasons preclude the current probe from being positioned at the substrate during normal operation. For the sake of accuracy the discharge current, which is directly related to the current density, is measured at varying current densities ranging from 0.1 - 0.8 mA/cm², with the probe positioned at its normal position near the ion source and also at the substrate area. Figure 6 shows how the current density varies at two different positions.

Another consideration regarding the measurement of ion current density is the angle of ion incidence. Trigonometry shows that the effective current density arriving normal to the substrate, \( j_1 \), is a fraction of the measured value from the probe:
\[ j_\perp = j_p \sin \phi \]

where \( j_p \) is the current density measured at the probe, and \( \phi \) is the angle of incidence or 20°.

5. Substrates

The substrates used are all 1 in diameter fused silica. Fused silica is chosen for two reasons: its lack of crystalline structure, and its relative purity over ordinary glass substrates. The amorphous nature of fused silica is important because no substrate crystalline orientation action will affect the orientation of the depositing film. The purity of the substrate eliminates the possibility of impurity-aided effects.

The substrates are cleaned first by brush scrubbing using a surface-active decontaminating detergent, followed by ultrasonic cleaning and a deionized water rinse. The samples are then mounted on the substrate platform and loaded into the vacuum chamber.
FIGURE 4. Schematic of experimental set-up.
FIGURE 5. Schematic of ion probe configuration.
FIGURE 6. Current density as a function of discharge current, as measured with ion probe positioned near the substrate and near the substrate ion source.
### TABLE 1. FIXED TARGET ION BEAM PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge Voltage, $V_d$</td>
<td>50 V</td>
</tr>
<tr>
<td>Accelerator Voltage, $V_{acc}$</td>
<td>-200 V</td>
</tr>
<tr>
<td>Beam Potential, $V_b$</td>
<td>1800 eV</td>
</tr>
<tr>
<td>Beam Current, $I_b$</td>
<td>40 mA</td>
</tr>
</tbody>
</table>

### TABLE 2. VARIABLE TARGET ION BEAM PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge Current, $I_d$</td>
<td>0.60 - 0.75 A</td>
</tr>
<tr>
<td>Accelerator Current, $I_{acc}$</td>
<td>2 mA</td>
</tr>
<tr>
<td>Cathode Current, $I_C$</td>
<td>3.5 - 5.5 A</td>
</tr>
<tr>
<td>Material</td>
<td>Sputtering Rate $\text{A/sec}$</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Nb</td>
<td>1.25</td>
</tr>
<tr>
<td>Al</td>
<td>2.14</td>
</tr>
<tr>
<td>Cu</td>
<td>2.38</td>
</tr>
</tbody>
</table>
### TABLE 4. FIXED SUBSTRATE ION BEAM PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge Voltage, $V_d$</td>
<td>50 V</td>
</tr>
<tr>
<td>Accelerator Voltage, $V_{acc}$</td>
<td>-100 V</td>
</tr>
<tr>
<td>Beam Potential, $V_b$</td>
<td>200 eV</td>
</tr>
<tr>
<td>Neutralizer Current, $I_n$</td>
<td>4 A</td>
</tr>
</tbody>
</table>

### TABLE 5. VARIABLE SUBSTRATE ION BEAM PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge Current, $I_d$</td>
<td>0.05 - 0.35 A</td>
</tr>
<tr>
<td>Accelerator Current, $I_{acc}$</td>
<td>≤1 mA</td>
</tr>
<tr>
<td>Cathode Current, $I_c$</td>
<td>4.5 - 5.5 A</td>
</tr>
<tr>
<td>Beam Current, $I_b$</td>
<td>0 - 2 mA</td>
</tr>
<tr>
<td>Current Density, $j_p$</td>
<td>0.2 - 0.65 mA/cm$^2$</td>
</tr>
</tbody>
</table>
METHODS OF ANALYSIS

Each grain in a polycrystalline sample usually has a crystallographic orientation unrelated to that of its neighbors. The orientations of these grains may be distributed randomly or they may tend to group, to differing degrees, about some particular orientation(s). The aggregation of grains toward a particular orientation defines the condition of preferred orientation or texture.

Preferred orientation is a common condition among metals and alloys that are produced by deformation (e.g. wire drawing or sheet rolling). This "deformation texture" is produced by the stresses and strains that accompany plastic flow. An orientation change continues until a texture is reached that is stable against any further plastic flow.

Preferred orientation is industrially important because of its effect on the macroscopic properties of materials. Each grain, or single crystal, may have anisotropic properties which vary along different crystallographic directions. It follows that materials having a preferred orientation may also have directional properties to varying degrees. Anisotropic properties may or may not be benefi-
cial. However, the ability to control the degree of preferred orientation, and thus anisotropy, is an advantageous tool that enables control over the macroscopic properties of materials, including mechanical, electrical, as well as magnetic properties.

Two methods for revealing the presence of a preferred orientation are x-ray and electron diffraction.

A. Pole Figure Method of X-ray Analysis

A very brief review of the stereographic projection is included to facilitate the discussion of pole figures. A more complete review can be found in reference 31.

The orientation of any crystal plane can be represented by a set of plane normals radiating from one point within the crystal. If this crystal is placed within a reference sphere constructed about this point in the crystal, the plane normals will intersect the surface of the sphere in a set of points known as the poles of the planes. For example, Figure 7 shows the location of the \{100\} poles of a cubic crystal in relation to its reference sphere. By the position of its pole on the reference sphere, the orientation of a plane can be determined.
A stereographic projection is a two-dimensional representation of the reference sphere. It is made by projecting a point light source from one end of any diameter of the reference sphere onto a projection plane normal to the other end of that diameter. Figure 8 illustrates this transformation process. Note that only one half of the reference sphere, the hemisphere directly opposite the light source, is represented on any stereographic projection. The hemisphere containing the light source will project outside the basic circle and extend to infinity.

A pole figure is a stereographic projection referenced with a specific orientation relative to the specimen. For a chosen set of crystal planes, a pole figure will show the variation of pole density with pole orientation. Thus, pole figures provide a complete representation of texture or preferred orientation.

In plotting a pole figure, the relations of Figure 8 must be kept in mind. Intensity variations on a single Debye diffraction ring are plotted on a single reflection circle in a pole figure. The diffraction ring will show an intense blackening when the reflection circle is cutting through regions where there is a heavy population of poles oriented for reflection. Correspondingly, lightly populated
regions will show up as areas of weak intensity on the
diffraction ring. To determine the complete texture repre-
sentation over an area, a series of reflection circles must
be plotted. By taking consecutive diffraction patterns with
the specimen tilted in increasing steps of 5°, a projection
or pole figure can be generated to display the texture of
the specimen.

As mentioned above, when a specimen exhibits preferred
orientation its Debye rings will be of nonuniform intensity
about its circumference, and may even be discontinuous if
a high degree of preferred orientation is present. This
nonuniformity occurs when a disproportionate number of
grains which would reflect the other portions of the ring
are either few in number or are simply not present. Non-
uniform diffraction rings are indicative of preferred
orientation.

Materials that are deposited by sputtering or evapora-
tion processes exhibit a "fiber texture" in the sense that
all crystal orientations have rotational symmetry about the
"fiber axis." The terminology stems from the observation
that the individual crystals in wire are oriented so that
most of the grains share a common crystallographic direction
parallel or nearly parallel to the wire axis. Therefore,
materials with grains that are rotationally symmetric about a common axis are said to have fiber texture.

To interpret pole figures exhibiting fiber texture, the pole corresponding to the fiber axis must be determined. The fiber axis in cubic specimens usually is \( \langle 111 \rangle \) for face-centered cubic and \( \langle 110 \rangle \) for body-centered cubic materials, corresponding to the lowest energy surfaces. (32)

In the x-ray pole figure method, the diffraction effects from thousands of grains are automatically averaged. The \((hkl)\) pole figure of a fine-grained material is constructed by analyzing the intensity distribution around the circumference of the corresponding \(hkl\) Debye ring.

The most convenient pole figure method is the Schulz reflection method, where a flat specimen is used and no corrections for absorption or changes in geometry during rotation of the sample are necessary from the center of the pole figure (normal to the surface of the sample) out to about 70°. Under these circumstances, the intensity of the diffracted beam is directly proportional to the pole density in the sample, without correction.

Schulz's reflection method uses an x-ray spectrometer
to measure the intensities of various areas of a pole figure. Intensity is recorded as a function of the angle between the fiber axis and the pole of the reflecting plane. Intensity variations can also be plotted on a stereogram for a qualitative description of the texture.

In Schulz's method, a reflection specimen is mounted in a goniometer head as in Figure 9 on plate C. The goniometer head is mounted by post P onto the axis of the x-ray spectrometer. This post supports two concentric rings, \( R_1 \) and \( R_2 \), that can be rotated through angles \( \phi \) indicated by graduations on the ring. The specimen is mounted on a circular plate, \( C \), which is supported by a second post, \( H \). Post \( H \) is adjustable so that the specimen surface is coincidental with the ring axis \( FF' \).

The x-ray beam is collimated by a series of slits which permit negligible divergence in both the vertical and horizontal directions. Slits \( S_1 \) and \( S_2 \) minimize divergence in the vertical direction. Wedges \( W_1 \) and \( W_2 \) limit the horizontal lengths of slits \( S_1 \) and \( S_3 \). Slit \( S_2 \) allows radiation to strike only a narrow band along the diameter of the specimen at the position of the ring axis \( FF' \). Wedge \( W_2 \) allows the entire width of a Debye ring to enter the counter, and slit \( S_3 \) sharply limits the length of the
arc that enters. By varying the angle $\phi$ data can be generated for one diameter of the pole figure. To obtain data for another diameter, the specimen is then rotated in its own plane by rotating plate C.

B. Transmission Electron Diffraction

Only the bare essentials of transmission electron diffraction will be discussed here. A more rigorous review of this topic can be found in references 33, 34, and 35.

The transmission electron microscope is, in many ways, similar to an optical microscope, except that its lenses are electromagnetic coils instead of glass. The fringing effects of these coils are used to focus an electron beam very precisely.

Electron microscopy requires a high vacuum chamber in which a collimated beam of electrons is accelerated, an electron source consisting of a hot filament which therm-ionically emits electrons, a condenser lens system, an objective lens, and a projection lens system composed of an intermediate electron lens and a projection lens. A ray diagram comparing the electron microscope during normal
image formation and during diffraction is shown in Figure 10.

When the transmission electron microscope is used for diffraction the strength of the intermediate lens is decreased, thus decreasing its focal length, until the focal length reaches a point where the objective back focal plane is conjugate to the intermediate lens image plane. The diffraction pattern appears at the intermediate image plane.

It is generally desirable to be able to compare the orientation of the sample with respect to its diffraction pattern. The magnetic field in the intermediate lens produces a rotation in the image relative to its diffraction pattern. Therefore, it is necessary to calibrate the relative angle between the electron image and the diffraction pattern as a function of the lens current. This was accomplished by using a crystal with a known habit, such as MoO$_3$, and measuring the angle between its edge and the diffraction spots corresponding to that edge. The possibility of a pattern inversion through a central spot should not be overlooked.

The diffraction pattern of a small-grained polycrystalline sample will consist of concentric Debye rings analogous to x-ray powder diffraction. The allowed reflections
for body-centered cubic lattices are \( h + k + l = \text{even} \),
and for face-centered cubic lattices are \( hkl \) all even
or all odd, thus allowing for crystal structure determin-
ation.

For polycrystalline samples that are not randomly
oriented the diffraction patterns may show subtle devia-
tions in relative ring intensities. Preferred orientation
can also cause discontinuous Debye rings, or arcs, where
the azimuthal spread in crystallite orientation about the
\( hkl \) direction is the angular length of the arc for a
ring of \( (hkl) \) indices. However, if preferred orientation
is not obvious in a diffraction pattern, tilting the sample
about an axis normal to the electron beam will often cause
the continuous rings to break into arcs.

Materials possessing fiber texture will show a diff-
raction pattern with certain rings systematically absent,
i.e. when the electron beam is coincident with the \( hkl \)
fiber axis only planes contained in the \( hkl \) zone contrib-
ute to the diffraction pattern. The condition of:

\[
hu + kv + lw = 0
\]

where \( uvw \) are the indices for the plane, must be satisfied.
Tables 6 and 7 list the reflections present in the body-centered cubic and face-centered cubic cases, respectively.
FIGURE 7. \(\{100\}\) poles of a cubic crystal. (Ref. 31)

FIGURE 8. The stereographic projection. (Ref. 31)

(Ref. 33)
FIGURE 10. Ray diagrams for double condenser, three-stage electron microscope. 
(a) normal image formation
(b) selected area diffraction 
Mode (b) is obtained from (a) by decreasing the focal length of the intermediate lens so as to image the pattern on back focal plane of objective lens. (Ref. 34)
<table>
<thead>
<tr>
<th>hkl</th>
<th>110</th>
<th>001</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>200</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>211</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>210</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>222</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>321</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

x corresponds to a visible ring
### TABLE 7. DIFFRACTION RINGS FOR FCC TEXTURED MATERIAL

<table>
<thead>
<tr>
<th>( hkl )</th>
<th>111</th>
<th>100</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>220</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>311</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>222</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>331</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>420</td>
<td></td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

\( x \) corresponds to a visible ring
RESULTS

The results of this study on the effect of low energy ion bombardment on the crystallographic orientation of niobium thin films can be categorized by the two methods of analysis used in this study:

(1) x-ray pole figure results

(2) transmission electron diffraction results

The x-ray diffraction method of analysis was used most extensively, and the pole figures enabled a semiquantitative analysis of the results. The results from transmission electron diffraction (TED) are used primarily to give qualitative support to the x-ray results.

A. Pole Figure Results

For all the niobium pole figures, the x-ray diffractometer was set to a 2θ value of 38.2° so that the intensities from diffraction off the (110) planes are recorded. This value is obtained from Bragg's Law, \( n\lambda = 2d\sin\theta \), using Cu Kα radiation.

1. Films Without Simultaneous Ion Bombardment
Figure 11 shows the pole figure for a niobium film deposited without simultaneous ion bombardment. The central spot indicates a material possessing fiber texture. The diffraction ring located 60° away from the central spot (as determined using a Wulff net) indicates a (110) fiber texture because of the 60° separation between 110 poles. The raw data for the pole figure shows the diffracted intensity as a function of the rotation and tilt of the sample. The uniform intensity of the 110 diffraction ring indicates that there is a random azimuthal distribution of the 110 poles.

2. Films With Ion Bombardment During Deposition

Figures 12, 13, and 14 show pole figures for samples bombarded with argon ions at current densities of 0.20, 0.30, and 0.35 mA/cm², respectively, as measured with the current probe placed near the substrate ion source. Although these pole figures show continuous rings of uniform intensity, inspection of the raw data corresponding to these plots reveals that at a tilt of about 60° small peaks are evolving. These peaks increase in height as the current density increases. However, the plotting apparatus is not sufficiently sensitive to resolve these small peaks into areas of darker shading.
Figures 15, 16, 17, and 18 show pole figures for niobium samples bombarded with current densities of 0.45, 0.55, 0.60, and 0.65 mA/cm², respectively. Nonuniform 110 diffraction rings are found in these plots suggesting a tendency for the 110 poles to aggregate about a preferred location. The diffraction peak heights increase with increasing current density indicating an increased degree of crystalline order at higher current densities.

The direction of incidence of the substrate ion beam with respect to the pole figure is as shown in Figure 15, and is consistent for all cases where there is substrate bombardment. The importance of the direction of ion incidence is revealed in a later discussion on why the higher intensity arcs shown in these figures occur in the same azimuthal regions about the diffraction rings.

The pole figure data is semiquantitatively summarized in Figure 19, which shows the degree of orientation as a function of the current density at the substrate, and the normal component of the current density which is calculated from the relation on page 38. The current density at the substrate is determined by using the measured current density near the ion source and Figure 6. The degree of orientation is estimated by averaging the five highest
peak intensities along the diffraction ring and normalizing this value by dividing it by the central peak intensity. The degree of orientation is generally found to increase with increasing current density, although the data contains much scatter. The degree of orientation can also be related to the ion to atom arrival rate ratio. Figure 20 shows the ion to atom ratio as a function of current density.

Figure 21 shows $Z$, the fraction of material resputtered by the substrate ion beam (in units of atoms removed/atoms arriving), as a function of current density. It is possible to estimate the sputtering yield from this plot by dividing $Z$ by the ion to atom ratio at a given current density.

3. Other Pole Figure Results

In order to obtain a better understanding of the influence of ion bombardment on film formation, a series of experiments were performed where films were bombarded after deposition or only during the first few minutes of deposition. A representative current density of 0.55 mA/cm$^2$ was chosen because this value was found to consistently result in a restricted fiber texture when concurr-
ently ion bombarded.

Figure 22 shows the pole figure for a film bombarded after deposition. Bombardment lasted for a duration equal to the deposition time. The continuous and uniform diffraction ring from this sample resembles that from an unbombarded sample.

A sample bombarded only during the first few minutes of deposition possesses a 110 pole distribution as shown in Figure 23. The initial 300 - 500Å of material adjacent to the interface was treated with ions, and a subsequent film was grown over the bombarded layer, with a thickness approximately five times greater than the treated layer. The pole figure shows high intensity arcs indicating that a restricted fiber texture is present in the film.

Figure 24 shows the pole figure for a sample that had substrate bombardment during the first half of the deposition time and no bombardment for the remaining half. This pole figure strongly resembles that from a sample that has had continuous ion bombardment.

B. Transmission Electron Diffraction Results
As mentioned earlier, these results are used primarily as qualitative evidence to support the existence of ion bombardment induced preferred orientation.

The diffraction patterns from samples bombarded at current densities of 0.55 and 0.60 mA/cm² are shown in Figure 25(a) and (b), respectively. For these samples, the electron beam was incident normal to the film surface. The varying diffracted intensities about the circumference of the rings indicate a preferred orientation is present. A clearer indication of preferred orientation can be found by tilting the sample so that the electron beam is no longer at normal incidence. Figure 26 shows diffraction patterns from a sample tilted at (a) -40°, and (b) +40°, with clearly visible discontinuities in the diffraction rings.
FIGURE 11. Pole figure for Nb without simultaneous ion bombardment. (#10268402, 3435Å)
FIGURE 12. Pole figure for Nb film with ion bombardment at $j = 0.20 \text{ mA/cm}^2$. (#11168402, 1790Å)
FIGURE 13. Pole figure for Nb film with ion bombardment at $j = 0.30\ mA/cm^2$.

(#11128401, 1445A)
FIGURE 14. Pole figure for Nb film with ion bombardment at $j = 0.35$ mA/cm$^2$.
(#11198401, 1870A)
FIGURE 15. Pole figure for Nb film with ion bombardment at $j = 0.45 \text{ mA/cm}^2$.
Note direction of ion incidence.
(#10308404, 1875Å)
FIGURE 16. Pole figure for Nb film with ion bombardment at \( j = 0.55 \) mA/cm\(^2\).

(#)11128404, 1745\(^\circ\)
FIGURE 17. Pole figure for Nb film with ion bombardment at $j = 0.60$ mA/cm$^2$. (#11138402, 2000Å)
FIGURE 18. Pole figure for Nb film with ion bombardment at $j = 0.65 \text{ mA/cm}^2$.
(#11138401, 2350Å)
FIGURE 19. Degree of orientation as a function of current density at substrate.
FIGURE 20. Ion/atom arrival rate ratio as a function of the current density at the substrate and the normal component of the current density.
FIGURE 21. Fraction resputtered as a function of current density at substrate.
FIGURE 22. Pole figure for Nb film bombarded after deposition at $j = 0.55$ mA/cm$^2$.

(#12268402, 2260A)
FIGURE 23. Pole figure for Nb film with only the first 300 - 500Å of material subjected to ion bombardment at $j = 0.55 \text{ mA/cm}^2$. (#12278402, 2410Å)
FIGURE 24. Pole figure for Nb film with ion bombardment during the first half of the deposition time at $j = 0.55$ mA/cm$^2$. (#12208404, 2240Å)
FIGURE 25. Diffraction patterns from Nb films with electron beam at normal incidence.
(a) $j = 0.55 \text{ mA/cm}^2$; (b) $j = 0.60 \text{ mA/cm}^2$. 
FIGURE 26. Diffraction patterns for Nb film bombarded at $j = 0.55 \text{ mA/cm}^2$. Sample was tilted (a) $-40^\circ$; (b) $+40^\circ$. 
DISCUSSION

In order to present a more effective discussion of the results of this investigation, the key observations will be briefly reiterated:

A restricted fiber texture is found to occur in niobium films subjected to low energy ion bombardment during deposition. The degree of orientation in the films increases with increasing current density up to about 0.65 mA/cm$^2$. The amount of resputtering also increases with current density. Films bombarded for a short period during the initial stages of film formation also possess a restricted fiber texture. However, films deposited before exposure to ion irradiation show only a fiber texture and no azimuthal preferred orientation. Finally, the higher intensity areas along the pole figure diffraction rings are found to consistently occur with a specific relation relative to the direction of ion incidence.

The higher degree of crystalline order in films with ion bombardment suggests a bombardment-induced enhancement of the adatom surface migration. The higher mobility of these atoms allows them to migrate to positions of lower
energy. At higher current densities the energy input into the surface is increased, thus increasing the level of surface mobility. This accounts for the increase in the degree of orientation with increasing current density.

The degree of orientation does not exceed about 70%, as shown in Figure 19. A current density of 0.65 mA/cm² measured with the current probe near the ion source, or about 0.42 mA/cm² at the substrate, corresponds to nearly 75% of the film removed by the substrate ion beam. The high resputtering rates at high current densities prohibit the growth of sufficiently thick films to do x-ray analysis.

Films subjected to ion bombardment after deposition are found only to possess a fiber texture with no restricted azimuthal preference. This suggests that ion bombardment affects the nucleation and growth kinetics of film formation, with low energy ion bombardment after deposition having little effect in inducing a restricted fiber texture. This observation supports Marinov's (12) results showing that a preferred orientation arises at the onset of the crystallization process due to ion bombardment, although without bombardment the crystallites are randomly oriented.

Continuous ion bombardment is shown to be unnecessary in maintaining a restricted fiber texture. This observ-
ation indicates that a sufficiently thick layer that has been treated with ions so that a preferred orientation is present, will serve as a template for subsequent arriving atoms. The template possesses enough crystalline order to influence the orientation of new nuclei. Films deposited with continuous ion bombardment possess a higher degree of order than films grown by the template method. However, this is probably due to the absence of the additional ion energy to promote surface migration with the template method.

It should be noted that the method used to arrive at a number to describe the degree of orientation is at most semiquantitative. A 50% degree of orientation should not be construed as 50% of all the grains being commonly oriented. However, the degree of orientation is meant to compare the diffracted intensities from the darker regions of the pole figure with the central peak intensity, which represents the total number of grains oriented with a common fiber axis.

The systematic location of the higher intensity areas along the diffraction rings with respect to the direction of ion incidence (as shown in Figure 15) can be explained by comparing the standard 110 projection in Figure 27 with
the pole figures in Figures 15 through 18. The higher intensity spots result from an aggregation of 110 poles, which appear to align with the direction of ion incidence. The [110] direction is a channelling direction in bcc materials such as niobium. Therefore, there is a strong indication that ion channelling between the 110 planes is directly related to the ion beam direction.

Channelling is usually associated with higher energy ions and monocrystalline materials. However, the results presented indicate that channelling may occur even at ion energies as low as 200 eV in a polycrystalline material with a grain size of about 200Å. The variation of sputtering yield with crystalline orientation provides a viable explanation for the alignment of the channelling direction with the ion beam direction.

The sputtering yield dependence on orientation is related to channelling in that directions where there is a minimum loss of energy per unit distance of the impinging ions will have a lower sputtering yield than unfavorably oriented directions. The criterion for minimizing ion energy loss is related to channelling on a "per grain" basis, where grains aligned favorably for channelling are less likely to be sputtered away. These grains will
survive and grow at the expense of the other grains. The variation of sputtering yield with orientation has been observed at ion energies as low as 100 eV for copper sputtering. (36) For the niobium experiments of the present investigation, the sputtering yield ranges from 0.45 to 0.60 atoms removed per incident ion for current densities of 0.30 to 0.40 mA/cm² measured at the substrate.

In Figures 14 through 18 it can been seen that the fiber axis, represented by the central spot on the pole figure, is tilted toward the direction of the ion beam. The fiber axis tilt increases with increasing current density. This effect can also be attributed to an alignment of the grains toward a more optimal orientation for ion channelling. Since the angle of ion incidence is fixed at 20° to the surface of the substrate, which is not a good channelling angle, the film compensates by tilting its grains, and thus its fiber axis, to a more favorable angle for channelling.

Studies of the effect of ion bombardment of copper and aluminum during deposition show no apparent influence of the ion beam on the crystalline orientation of the films. These low melting temperature materials are probably annealed by the ion beam so that no preferred orientation occurs.
FIGURE 27. Standard 110 projection.
CONCLUSION

The effect of simultaneous low energy ion bombardment during the deposition of niobium thin films has been investigated. At an ion energy of 200 eV and an incident angle of 20° to the plane of the substrate, ion bombardment has been found to result in films with a restricted fiber texture.

The degree of orientation in the films increases with increasing current density, but does not exceed about 70% at a current density of 0.42 mA/cm² measured at the substrate. This is due to the high resputtering rate at high current densities, which prevents the formation of sufficiently thick films for x-ray analysis. The higher degree of crystalline order in films with ion bombardment suggests a bombardment-induced enhancement of surface migration.

Films bombardèd only during the initial stages of growth are found to also possess a restricted fiber texture. This indicates that bombardment can produce a template with enough crystalline order to influence the orientation of subsequently formed nuclei.
Finally, the direction of ion incidence is found to coincide with the 110 channelling direction. The orientation dependence of the sputtering yield is the probable cause for this effect. The sputtering yield is higher for non-channelling orientations, and therefore grains with an unfavorable orientation are more likely to be resputtered by the substrate ion beam. Grains oriented favorably for channelling will survive and grow.
The area of ion-surface interactions and the effect of ion bombardment during film growth is an interesting one with numerous topics for investigation. In this study a fixed ion energy and angle of incidence was used. It may be of interest to study the effects of different beam energies on the crystalline state of the resultant film. Varying the angle of ion incidence may reveal that an optimum angle exists which not only aligns the channelling direction with the beam direction, but also renders the highest degree of crystalline order.

The study of different materials may prove to be a more difficult task. Materials having low melting temperatures, such as copper and aluminum, are found to be annealed by the substrate ion beam so that no restricted fiber texture occurs.

The study of the influence of ion bombardment on epitaxial film growth is another interesting possibility that is already being investigated in many laboratories.

Finally, the ultimate goal is to understand the mech-
anism responsible for all the observed effects, and therefore have a firm grasp on the physics of how to control material properties through ion bombardment.
REFERENCES


