Stellingen bij het proefschrift

Metal nitrides for superconducting tunnel detectors
Nikolai Iossad

1. Ondanks claims in de literatuur biedt het gebruik van een ongebalanceerde sputterbron geen voordeel in vergelijking met een gebalanceerde sputterbron.

2. Magnetron sputterbronnen moeten door de fabrikant gecertificeerd worden aan de hand van filmstress-sputterdruk curves voor nieuwe en geërodeerde targets.

3. Inhomogene oxidatie van de Al laag in gestapelde [Nb/Al-AlO₅/Nb]₇ juncities veroorzaakt een substantiële verandering van de weerstand van AlOₓ tunnelbarrières geoxideerd onder dezelfde zuurstofdruk.

4. Een adequate investering in de ontwikkeling van NbN leidt tot microgolfeigenschappen van dit materiaal die vergelijkbaar zijn met (Nb,Ti)N.
   4-1. Dit proefschrift, hoofdstuk 2.

5. Het gebruik van zware edelgassen tijdens het groeien van lagen met ion-assistance veroorzaakt geen extra stress, in vergelijking met argon, en leidt tot lagen met nieuwe eigenschappen.

6. Een scherend invallend elektronenbombardement kan gebruikt worden om oppervlaktediffusie tijdens de groei van de lagen te stimuleren.

7. Een modulaire samenstelling van een proefschrift is beter dan een “compleet verhaal.”

8. De Japanse industriële ontwikkelingsbenadering “Pak het beste en maak het beter” leidt niet altijd tot een beter product.

9. In tegenstelling tot het Nederlands hebben komma’s in de Russische taal de functie van zinsbouw.

10. Een jonge mentaliteit maakt mensen meer geneigd risico’s te nemen en bijgevolg een vol leven ouder.

11. Niet de promotor maar de promovendus moet na de verdediging van het proefschrift een sabbatsverlof van 6 maanden krijgen.
Propositions to the thesis

Metal nitrides for superconducting tunnel detectors

Nikolai Iossad

1. In contrast to claims in the literature unbalanced magnetrons have no practical advantage over balanced sources.
   1-2. This thesis, Ch. 4.

2. Magnetron sputtering sources should be certified by the supplier with stress-pressure curves for fresh and eroded target surfaces.
   2-1. This thesis, Ch. 4.

3. Inhomogeneous oxidation of the Al layer in [Nb/Al-ALO\textsubscript{x}/Nb]\textsubscript{N} stack junctions causes a substantial variation in the resistance of ALO\textsubscript{x} tunnel barriers oxidized under the same conditions.

4. An adequate investment in developing suitable NbN would lead to comparable microwave properties compared to (Nb,Ti)N.
   4.1. This thesis, Ch. 2.

5. Utilization of heavy noble gases during film growth for ion assistance will not cause extra compressive stress compared to Ar and will result in films with new properties.

6. Grazing incidence bombardment of electrons can be used to stimulate surface diffusion during film growth.

7. A modular structure of the thesis is better than “a complete story” structure.

8. The Japanese industrial development approach “Take the best and make it better” does not necessarily lead to a better product.

9. Comma’s perform the task of sentence construction in the Russian language in contrast to Dutch.

10. A young mentality makes people willing to take risks and as a consequence a full life older.

11. Ph. D. students should be granted a 6 month sabbatical leave after the thesis defense, instead of supervisor.
Metal Nitrides for Superconducting Tunnel Detectors

Nikolai Iossad
Metal Nitrides for Superconducting Tunnel Detectors

Proefschrift

Ter verkrijging van de graad van doctor aan de Technische Universiteit Delft, op gezag van de Rector Magnificus prof. dr. ir. J. T. Fokkema, voorzitter van het College voor Promoties in het openbaar te verdedigen op Maandag 9 september 2002 om 13:30 uur

door Nikolai Iossad
Master of Science in Physics
geboren te Moskou
Dit proefschrift is goedgekeurd door de promotors
Prof. dr. ir. T. M. Klapwijk

Samenstelling promotiecommissie

Rector Magnificus       voorzitter
Prof. dr. ir. T. M. Klapwijk Technische Universiteit Delft, promotor
Prof. H. Rogalla         Universiteit Twente
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Prof. dr. ir. S. van der Zwaag Technische Universiteit Delft
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Prof. dr. H. W. Zandbergen Technische Universiteit Delft
Prof. dr. B. J. Thijsse   Technische Universiteit Delft

Dr. S. N. Polyakov (Moscow State University) heeft als begeleider in belangrijke mate
aan de totstandkoming van het proefschrift bijgedragen.

**DIMES**

Part of this work has been performed at DIMES, the Delft Institute of Microelectronics
and Submicron Technology

**SRON**

This work has been performed in close collaboration with SRON, National Institute for
Space Research

Plan view TEM image of NbN film is illustrated on the cover.

Iossad, Nikolai
*Metal nitrides for superconducting tunnel detectors / Nikolai Iossad*
ISBN 90-77017-96-8
Keywords: Superconductivity / Metal nitrides / Magnetron sputtering
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Chapter 1

Justification of materials choice

1.1 History of the development of low $T_c$ superconducting electronics

The intense development of superconducting electronics has begun with the discovery of the Josephson effect in 1962 [1,2]. The very first superconductor-insulator-supercollider (SIS) junctions were produced in the early 60's on the basics of soft metals like Sn, Pb, or In and thermally oxidized barriers [3]. Typical junction size was 100×100 μm² and critical current densities were in the range of 1-10 A/cm². These junctions were very easy to handle, and showed excellent correspondence to theory. IBM has achieved further progress in junction development in the 70's [4-7]. The bottom electrode was made of PbInAu alloy, tunnel barrier was created by oxidation of a bottom electrode in the RF-discharge, and a top electrode was made of PbIn or PbBi. “Lead IBM technology” technology was the first to provide reproducible junctions. However these junctions showed low stability for thermocycling down to helium temperatures and low mechanical durability. Moreover the junction parameters have been changing throughout the storage at room temperature. Further development required utilization of hard materials, mainly transition metals like Nb. These films have good stability and high $T_c$. The main difficulty at that time was to produce pure Nb films, since the properties of these films are very sensitive to the background pressure of water, oxygen, oil, etc. The tunnel barrier was made by the oxidation of the bottom Nb or V electrode [8-9]. However the quality of the junctions produced in this way was marginal, since the junctions had high specific capacitance values and leakage currents. The main problem of the niobium oxide tunnel barriers is that they consist of various niobium oxides, while only Nb₂O₅ is a dielectric (NbO has a metallic conductivity for instance) [10].

The first attempts to produce artificial tunnel barriers took place in the early 80's. A number of materials (amorphous Si, Al₂O₃, SiO₂, Al₂O₃, etc.) have been tried out [11-13]. As a result Nb/Al-AlOₓ/Nb try-layer has become the “working horse” of superconducting technology of our days [14]. These junctions have excellent stability and properties. The tunnel barrier is made by an oxidation of Al layer in an atmosphere of pure oxygen under the pressure of about 1 Pa. This thin oxide layer is very stable, even the direct sputtering of Nb top electrode does not damage it. These SIS junctions have a very low level of intrinsic noise and very low switching times between
superconducting and normal state (≈ 1 ps). This technology enabled successful implementation of a broad spectrum of superconducting electronic devices with record characteristics: highly sensitive high frequency receivers of the mm and sub-mm range, integrated receiver comprising heterodyne, mixer, and antenna one chip, SQUID amplifiers and magnetometers, and digital devices for the super fast data processing [15-24].

Further development of the junctions can be associated with production of sub-micrometer size junctions, quality control of the layers and interfaces, searching for the candidate with higher $T_c$ compare to Nb that can substitute Nb films in junction production [25-34]. NbN and (Nb,Ti)N films are the most likely candidates at the moment. High quality SIS junctions were produced using these materials and artificial barriers of AlN and MgO [35,36]. The best results were obtained using NbN films grown epitaxially on MgO wafers. These NbN/AlN/NbN junctions show the best results at present.

1.2 Pushing the operation of the SIS mixers towards THz frequencies

The work described in this thesis is the part of European Space Agency project that aims to develop a novel instrument for radio astronomy. The main purpose of this project is the deployment of a radio astronomical facility (Herschel) on the orbit of the Earth [37]. Herschel will enable to perform observations, which are not limited by the atmosphere transmittance. In particular this mission will provide an opportunity for the scientists to explore the universe in the frequency range above 900 GHz, which is practically impossible to perform with the help of the ground based facilities because of atmospheric cut-off. SIS heterodyne receivers are the best tools for this task. Therefore, pushing the operation of these devices towards THz frequencies is an essential element of this program.

High nonlinearity of a SIS junction quasi-particle current is used in sensitive receivers of mm- and sub-mm-ranges. The definition of the most important junction parameters is illustrated in Fig. 1.1. The gap voltage $V_g$ is determined at the middle of a sharp rise of a quasi-particle current. $R_{sg}$ is junction resistance below $V_g$, $R_n$ is junction resistance above $V_g$. Gap smearing ($\Delta V_g$) determines the width of a quasi-particle current rise at gap voltage. It has been shown that SIS mixers can provide the frequency conversion with amplification and noise level close to quantum limit (hf/k), while all classical mixers have conversion coefficient less than unity. This frequency conversion is possible in so called “quantum regime”. The criterion of this regime is $\Delta V_g < hf/e$ ($f$ heterodyne frequency) [38]. This condition is the bottom frequency limitation for the “quantum regime”. The current below the gap voltage (sub-gap leakage) is the other important parameter. The performance of the SIS mixer degrades strongly with the increase of this parameter. In most of the cases a value $R_{sg}/R_n>10$ is needed [38]. Increase in the sub-gap leakage results in a suppression of the conversion coefficient of SIS mixer and extra noise. Gap voltage an important parameter as well, since it determines the upper frequency limit for SIS utilization ($f_{\text{U}}=2eV_g/h$) [38]. In addition, junctions with high current densities and low sub-gap leakage currents enable to produce mixers with a broad instantaneous bandwidth [39].
Fig. 1.1. Typical voltage current characteristic of a quasi-particle branch of SIS junction. $R_n$—normal resistance, $V_g$—gap voltage, $\Delta V_g$—gap smearing, $R_{sg}$—sub-gap resistance.

The lay-out of an integrated circuit (IC) containing SIS junctions integrated in a strip-line is illustrated on Fig. 1.2. The device is made by conventional means of planar technology widely used in semiconductor industry. SIS junction is formed on quartz wafer buffered with $\text{Al}_2\text{O}_3$ layer and integrated in (Nb,Ti)N strip-line. The strip-line enables the coupling of microwave radiation to the SIS junction. Utilization of superconductors in strip-lines imposes its own criterions on materials used for this purpose, since SIS mixers require low loss tuning elements. The Mattis-Bradeen theory

Fig. 1.2. Lay-out and cross-sectional view of Nb/Al-$\text{AlO}_x$/Nb SIS junction integrated in (Nb,Ti)N/Al strip-line. (Modified from ref. 21.)
highlights two critical parameters ($T_c$ and resistivity in a normal state), determining the losses in superconducting strip-lines [40]. Microwave losses have a dramatic increase at frequencies above $2\Delta/h$, where $\Delta$ is the energy gap of the superconductor. Moreover, film resistivity just above transition temperature has to be as low as possible in order to minimize the microwave losses as well. In addition, increase in film resistivity results in an increase in magnetic field penetration depth. This parameter determines the penetration of microwave radiation in the superconducting strip-line. The penetration of the microwave radiation through the metal layer of the strip-line causes extra radiation losses. Moreover it is very difficult to calculate such a structure. Therefore the thickness of the film used in a strip-line has to be higher than magnetic field penetration depth. Utilization of the films with big magnetic penetration depth requires thick metal layers, which are difficult to integrate in the IC.

Development of SIS mixers imposes certain requirements on wafer materials as well. Both quasi-optical and wave-guide mixers require low-loss wafers. Moreover, wave-guide mixers require substrates with low dielectric constant, because the wafer creates a capacitive shunt for the microwave radiation in the wave-guide. Therefore the choice is reduced to quartz wafers in this case.

1.3 Strip-line material selection

As it has been mentioned in the previous paragraph, the Mattis-Bardeen theory imposes the upper frequency limitation for utilization of a superconductor as a strip-line material. According to this theory, the upper frequency limit for Nb is in the vicinity of 700 GHz. Thus a development of THz detectors based on SIS junctions requires that a superconductor with higher gap frequency has to be used in the mixer design. Several groups of low transition temperature superconductors are possible candidates: Chevrel phases, A15, B1, etc. However, the problem of obtaining a high quality films by sputter deposition at ambient substrate temperature is not a trivial one. For this application we need reproducible films with the lowest possible resistivity, the highest possible transition temperature ($T_c$), and intrinsic stress that does not cause peeling of the film layers or photoresist. As an example Nb$_5$Sn needs to be deposited on a high-temperature substrate ($T_c\geq700^\circ$ C) or to have a high-temperature annealing after deposition to obtain good superconducting properties. Chevrel phases or C15 compounds can be produced only at high temperatures as well. In contrast, B1 type nitrides of transition metals have been a matter of strong interest for the last 30 years among the superconducting community. The primary advantage of these materials is the simple way of thin film production like reactive magnetron sputtering at ambient substrate temperature. This enables a broad range of device applications, including RSFQ, SQUID, and THz mixers [28, 35, 36, 41-44]. Films of TiN deposited by reactive magnetron sputtering at ambient substrate temperature show the lowest resistivities, while films of NbN the highest $T_c$ [28-30]. Therefore, magnetron sputtering of NbN and (Nb,Ti)N films are broadly investigated in this thesis. Taking into account the data published in ref. 45, which show similar properties for (Nb,Zr)N and (Nb,Ti)N thin films, (Nb,Zr)N are investigated as well. Nb(N,C) films have one of the highest $T_c$'s among nitrides and carbides of transition metals [46], but the concerns related to compatibility of methane based process with ordinary Nb based technologies restrict our research to the nitrides.
1.4 Tunnel barrier material selection

The development of SIS junctions on the basics of transition metal nitrides requires utilization of artificial tunnel barriers. Direct plasma oxidation of the metal nitride layer will obviously lead to the same sub-oxide problem as in the case of Nb electrodes. Utilization of Al-AlOx tunnel barrier results in poor junction quality as well, presumably due to poor interface quality of metal nitride and aluminum [47]. Artificial barriers of AlN and MgO are the most promising candidates at the moment [35,36].

Nb based SIS junctions can be used in THz mixers as well, since the frequency limitation in this case is two times higher compare to the frequency limitation for the Nb based strip-lines [48]. These junctions can be used in SIS mixers up to 1.2-1.4 THz depending on junction quality. The most important achievement in Nb SIS junction development has been recently reported by Bumble et al. Utilization of AlN tunnel barrier created by plasma nitridation enables to produce excellent junctions with high critical current densities. Successful implementation of AlN tunnel barriers in various types of tunnel junctions initiated experimental investigation of this problem described in the last two chapters of this thesis.

P. S. Dear colleagues, this thesis has a modular structure. You may start reading from any chapter.

References


37. http://www.sron.nl
Chapter 2

Experimental comparison of materials

2.1 General properties of transition metal nitrides

The nitrides of transition metals are famous for a lot of remarkable properties [1]. Extremely high hardness of these metals makes them excellent materials for tool coating. The typical microhardness values are in the interval of 2000 and 3000 kg/mm$^2$ – values, which lie between those of sapphire and diamond. The second striking point is the high melting points of these materials. The typical melting temperatures are in the band of 2000$^\circ$ and 3000$^\circ$ C and approximately equal or higher than the melting temperatures of the parent transition metal elements. One of the most important features of the nitrides is their defect structure. Understanding the structure of defects in particular nitride compound is the key element of understanding of its thermodynamic, mechanical, electrical, magnetic, superconducting, etc. properties. Ideal stoichiometry is a rare case in the world of nitrides. As usual these materials have vacancies on metal or nitrogen sublattices or on both of them due to the lack of one of the elements. The vacancies may exist in considerable concentrations even in stoichiometric compounds. The phases exist over a broad composition ranges and appreciable vacancy concentrations (up to 50 at. %) can exist on nonmetal lattice sites with lesser on metal atom lattice cites. The vacancies on the nonmetal sites tend to form long-range order in the case of high concentrations. Because of possibilities of vacancies ordering in the defect structures, the crystal chemistry of carbides and nitrides is complex. Nitrogen as much smaller atom compare to the atoms of transition metals is always interstitially located. The crystal structure of nitrides can be described as the geometric arrangement of interstitial atoms and vacancies on a relatively simple metal lattice. This approach is typically used for the description of the vacancy defect structures. The other approach is to describe these materials as geometric arrangement of coordination polyhedra. One of the most frequent is an octahedral grouping of metal atoms around the nitrogen atom. While many crystal structures of nitrides are complex, most of them can be reconstructed from only a few different coordination polyhedra. Bonding in these compounds consists of complex combination of localized metal-to-metal and metal-to-nonmetal interactions resembling covalent, metallic and small ionic bonding. The metal-to-nonmetal bonding is favored by the octahedral arrangement of metal atoms around the nitrogen one, on the other hand the presence of nonmetal atom in the center of this structure results in the increase of the strength of metal-to-metal bonds. The most difficult problem is the variation of bonding
with defect structure. Similar problem in TiO has been calculated and the solution indicates major changes in the bonding with the changes in the defect structure. Nitrides of transition metals are typically metallic in their magnetic, electrical, and optical properties. Most of these properties are close to the parent metals. Electrical and magnetic properties are very sensitive to the structural defects. For example, electrical resistivities of these materials are mainly determined by point defects in the matrix rather than the concentration of electrical current carriers. Superconducting properties of transition metal nitrides are very well studied by now. Most of the phases are superconductors with $T_c$ above 10 K. High $T_c$ of the nitrides of transition metals is mainly determined by strong electron-phonon interaction temperatures and high Debye temperatures. There is an interesting correlation between the crystal structure and $T_c$. All nitrides of transition metals with high $T_c$'s have the octahedral coordination polyhedron. For example phases of NbN, (Nb,Ti)N, (Nb,Zr)N with highest $T_c$'s have B1 crystal structure with octahedral grouping of metal atoms around the nitrogen atom (Fig. 2.1), and superconductivity exists in these alloys in the magnetic fields over 200 kG and current densities of $10^5$ A/cm² are observed even at fields of 100 kG. This feature makes these materials excellent candidates for the cables for superconducting magnets. The absence of high peak of density of states (DOS) at Fermi level makes the $T_c$ insensitive to matrix defects caused by preparation or irradiation and therefore allows the utilization of these materials for accelerator cavities. The deviation from stoichiometry causes a moderate reduction of the $T_c$, associated with reduction of DOS at Fermi level and Debye temperature.

![Octahedral grouping](image)

**Fig 2.1.** B1 crystal structure. Octahedral grouping of metal atoms around nitrogen is shown by dashed lines.

### 2.2 Film deposition and characterization

Films of nitrides are deposited by reactive magnetron sputtering in a Nordiko-2000 sputtering system. This system is equipped with four DC magnetrons (two of these sputtering sources have the RF discharge option), one RF-diode sputtering source, and the load-lock system (Fig. 2.2). The substrate table has two plates one water-cooled and the other with IR heater. RF discharge can be applied to both of them. This option allows to clean and activate the substrate surface prior
Fig 2.2. Plan-view of the Nordiko-2000 sputtering system. 1 and 10 – view ports, 2 - load-lock, 3 - Al RF-diode sputtering source, 4 - Nb DC sputtering source, 5 - Al DC-RF sputtering source, 6 - Au DC sputtering source, 7 - CaF$_2$ IR view port, 8 - NbTi DC-RF sputtering source, 9 - gas injection port.

to film deposition and to stimulate surface diffusion during film growth. The substrate temperature can be monitored by the pyrometer through the special CaF$_2$ window. The distance between the substrate and the sputtering source can be set in the range of 4-8 cm. The sputtering sources are located above the substrate. This system has 1500 CTI cryo-pump, which provides 2·10$^{-5}$ Pa base pressure and a pumping rate of 1500 l/s. Gas injection and control system together with the throttling valve determine the gas pressure in the main chamber. All gases, used for processing, are 99.99% at. % pure. The purity of all targets is 99.8 at. % or better. Alloy targets of NbTi and NbZr are used for the deposition of solid solutions of transition metals. The substrates are fixed to a copper chuck with diffusion pump oil, which is maintained at 10$^\circ$ C to stabilize the substrate temperature.

The stress in the films is evaluated by measuring the deflection of the wafer before and after film deposition with a profilometer. The stress value is calculated with the help of Stoney's equation [2],

$$\sigma = \frac{1}{6R} \frac{E}{(1-v)} \frac{D^2}{d}$$

where $E$, $v$, and $D$ are the Young's modulus, Poisson's ratio, and thickness of the substrate, respectively. $E/(1-v)$ equals to 94 Gpa for glass wafers [3], $d$ is film thickness, and $R$ is the radius of curvature of the substrate, calculated from the deflection measurement.

All films used for resistivity and $T_c$ measurements were deposited on the wafer covered by photore sist mask. After the lift-off procedure the structure for the sheet resistance measurements was formed and the thickness of the sample was measured. Afterwards the sample carrier with bonded samples was inserted in the vacuum dipstick and cooled down to 4.2$^\circ$ K temperature in tank containing liquid helium. The temperature
sweep was performed by sending the current through the heating resistor. $T_c$ is evaluated from the dependence of film resistivity on temperature. Low temperature film resistivity was measured at 20° K. This value is illustrated on all of the plots, since it is more informative from the prospective of the RF losses. Residual resistance ratio (RRR) is determined as the ratio of film resistivity at room temperature and 20° K.

In-plane film homogeneity is estimated by the measurement of the ac-magnetic susceptibility [4]. The thermo-cycling technique is the same as in the previous paragraph. This measurement is performed by placing the sample between excitation and receiving coils (Fig. 2.3). The e.m.f. in the receiving coil is determined by the shielding of magnetic field by the superconducting fraction of the film. Therefore the dependence of susceptibility versus temperature will provide information about the spread of transition temperatures of the different fragments of the film, compare to the simple resistivity vs. temperature measurements.

![Fig. 2.3. Circuit diagram of the ac- susceptibility measurement set-up. $I_b$ - ac current source, $L_1$ - excitation coil, $L_2$ - receiving coil, $V$ - nano-voltmeter.](image)

X-Ray diffraction (XRD) data is collected using a Rigaku D/max-Rc diffractometer equipped with a thin-film diffractometer, pole-figure goniometer, 12 kW X-ray generator of Cu Kα radiation, and a graphite crystal–monochromator. Two techniques for XRD film examination were used for film characterizatoin. The conventional $\Theta$-2$\Theta$ scans in the range of 15-120° are used for phase identification and preliminary sample analysis. In order to simplify the measurements and reduce the data collection time azimuth scans of [111] reflections at tilt angle c. a. 54.7° are used to examine epitaxial relation [5,6]. This scan is equivalent to a circular trace on a stereographic projection (Fig. 2.4). Cross-sectional samples are prepared by a standard technique - mechanical thinning down to 30 μm, followed by ion milling using a Gatan 600 Duo Ion Mill. The specimens are examined with a Philips EM430ST transmission electron microscope (TEM) operated at 200kV.

### 2.3 Comparison of thin films of transition metals nitrides

In order to select the best material for THz mixer development, 500 nm thick films of different compositions are sputtered on glass wafers. The optimum ratio of Nb and Ti in the sputtering target is determined by comparing the maximum possible $T_c$ of (Nb,Ti)N films sputtered from targets with different compositions. The NbTi target with 30 at. % Ti content is selected for further studies, since it provides the highest possible Ti content in the deposited films without $T_c$ degradation (Fig. 2.5). A NbZr alloy target with 30 at. % Zr for is used as well for the studies of (Nb,Zr)N.
Fig 2.4. Stereographic projection for a cubic lattice. [001] axis is perpendicular to a projection plane. The trace of an azimuth scan is shown by the dashed line.

Fig. 2.5. $T_c$ dependence of the (Nb,Ti)N films deposited on glass wafers at ambient substrate temperature versus Ti content in the sputtering target.

The properties of NbN, (Nb,Ti)N, (Nb,Zr)N are illustrated on Fig. 2.6 and Fig. 2.7. The lower edge of the pressure range is determined by an increase in compressive stress (Fig. 2.7), while upper pressure limit is determined by an increase of film resistivity, which makes the films unacceptable for device production. Nitrogen injection is optimized to achieve the highest possible $T_c$ for each sputtering pressure. It is found that $T_c$ has only a moderate dependence on pressure, while film resistivity increases sharply at high pressures. The intrinsic stress curves
show a normal behavior, with a rapid increase in compressive stress at low pressures. The RRR is in the vicinity of unity for all the films, indicating that film resistivity is determined by crystal defects. XRD analysis reveals that all films have a B1 crystal structure. The ratio of (200) and (111) XRD peaks increases with the decrease of the sputtering pressure for all materials (Fig. 2.7).

The properties of 500 nm thick (Nb,Ti)N and NbN films sputtered on (100) MgO wafers are compared as well. (Nb,Zr)N films are not included in this experiment because of their low $T_c$. The results of the XRD azimuth scanning (typical for all films on MgO wafers) are illustrated on Fig. 2.8. The presence of 4 well pronounced peaks on film XRD azimuth scan of [111] reflections and their one to one correspondence to the same scan of the substrate indicates that the film is grown epitaxially on a substrate ( (100)MgO || (100)(Nb,Ti)N, (111)MgO || (111)(Nb,Ti)N ).
Fig. 2.7. Ratio of [111] and [200] XRD peak intensity and intrinsic stress, of (Nb,Ti)N, (Nb,Zr)N, NbN films deposited on glass wafers at ambient substrate temperature.

Fig. 2.8. XRD [111] peak intensity versus azimuth at tilt angle c. a. 54.7° of the film (top curve) and the substrate (bottom curve).
Typical values of full width at half maximum (FWHM) of [200] reflections of films grown on MgO substrates are in the interval of 0.8°-1°. Similar value for MgO wafers is only 0.1°. High FWHM values of the films compare to the substrate value are caused presumably by misfit dislocations. (The lattice misfit for (Nb,Ti)N is 3%. The lattice misfit for NbN is 4%.) Film properties are illustrated on Fig. 2.9. Nitrogen injection is optimized to produce maximum $T_c$ for every sputtering pressure. In general, $T_c$ and RRR have only a moderate dependence on sputtering pressure, while film resistivity increases considerably at high pressures. It is believed that the degradation in film properties at high pressures is due to the development of voids between the blocks in the mosaic structure and an increase in the quenched-in vacancy concentration. In contrast with the films sputtered on glass wafers, a flattening of the curves at low pressures is observed, which is a clear advantage from the prospective of film

![Graph showing $T_c$, film resistivity, and RRR vs. sputtering pressure (mTorr).](image)

**Fig. 2.9.** RRR, film resistivity, and transition temperature of the (Nb,Ti)N, NbN films deposited on MgO wafers.
reproducibility.

NbN films deposited on Si wafers covered by rf-sputtered MgO (100 nm thick), show a more pronounced [200] XRD peak and lower resistivity when compared with the NbN films sputtered on bare Si wafers under the same deposition conditions. However since a $T_c$ improvement in NbN films by utilizing MgO under-layers is not observed this technological approach is not studied extensively.

2.4 Homogeneity analysis

Because the magnetic field penetration in (Nb,Ti)N films is almost equal to the typical thickness of the layers ($\approx 300$ nm) that are being used in strip-lines for THz mixers, film homogeneity is a very important issue. Fig. 2.10 illustrates the $T_c$, film resistivity, and ratio of the

![Diagram]

**Fig. 2.10.** Relative XRD peak intensity, film resistivity and transition temperature of the (Nb,Ti)N films, deposited on MgO, sapphire, Si, and glass wafers.
XRD [111] and [100] peaks for different (Nb,Ti)N film thickness and wafer materials. All films are deposited under 6 mTorr sputtering pressure and 300 W DC power, since these conditions provide the best film properties from the perspective of mixer development. Both film resistivity and $T_c$ have only a moderate dependence on film thickness. However, since $T_c$ determines the frequency cut-off of a micro-wave strip-line, this data is important for device characterization. A similar picture was observed previously by Wang et al. for NbN films [7,8].

XRD analysis shows no considerable difference in the XRD patterns of 300 nm thick (Nb,Ti)N films deposited on Si, glass, or sapphire wafers, when compared with the changes in XRD patterns caused by a change in the sputtering pressure of 1 mTorr. This indicates that wafer material plays only a minor role in the film growth, compared to other technological parameters. All films deposited on Si, glass and, sapphire wafers show a more pronounced [200] peak for thinner films (Fig. 2.10). Similar observation of competitive growth in TiN films was reported by L. Hultman et al. [9,10].

Cross-sectional TEM analysis of 150 nm thick (Nb,Ti)N film on sapphire wafer (Fig. 2.11) shows a rapid increase in the grain size with film thickness and a more pronounced columnar structure for the upper layers of the film. This data is in good correlation with the broadening of the XRD peaks for thin films. The flattening of the relative XRD peak intensities curves for 250-300 nm thick films (Fig. 2.10) indicates that film growth reaches an equilibrium at this thickness, which is compatible with the thickness of the (Nb,Ti)N layers used in mixer production. These changes indicate that the film crystallinity improves with the film thickness. In the other words, the growth mode has a tendency to change from the ZT to the Z2 structural zone as the thickness of the film increases [7]. This results in an increase in $T_c$ and a reduction in film resistivity with film thickness, for films deposited on Si, glass, and sapphire substrates. It is believed that misfit dislocations cause the $T_c$ degradation with film thickness for the epitaxial films deposited on MgO wafers.

A certain attempt to explain strong dependence of $T_c$ on film thickness was undertaken by V. Z. Kresin and V. M. Pan et al. [11, 12]. They propose the explanation on the basis of McMillan proximity effect model in assumption that the top layer of the films is oxidized and therefore the films consist of two superconductors with different $T_c$'s or a normal metal and superconductor. This approach is doubtful because $T_c$ reduction occurs at the film thickness which is an order of

![Cross-sectional TEM view of (Nb,Ti)N film.](image)

Fig. 2.11. Cross-sectional TEM view of (Nb,Ti)N film.
magnitude higher than the coherence length of these materials (3-4 nm).

The dependence of intrinsic stress on film thickness is also examined, since it shows a nonlinear behavior versus thickness, and this may cause a lattice distortion responsible for the $T_c$ degradation. Fig. 2.12 illustrates the intrinsic stress and $T_c$ dependencies on film thickness for (Nb,Ti)N films deposited at 6 and 9 mTorr. As it can be seen, the $T_c$ degradation for thin films does not correlate with the stress curve for the almost stress-free film. Thus, it is concluded that intrinsic stress does not cause the $T_c$ degradation of thin films.

The in-plane film homogeneity is estimated from ac susceptibility data. Fig. 2.13 illustrates the ac susceptibility versus temperature for the 300 nm thick epitaxial film deposited on MgO

**Fig. 2.12.** $T_c$ and film stress versus (Nb,Ti)N film thickness for the films sputtered under pressure of 6 and 9 mTorr on glass substrates.

**Fig 2.13.** AC magnetic susceptibility of (Nb,Ti)N films on glass (left curve) and MgO (right curve) wafer.
wafer and non-epitaxial film deposited on glass wafer. As seen from the Fig. 2.13 both films have sharp transition width (≈ 0.2 K). No specific steps corresponding to the phases or regions with different $T_c$ are observed on this curve. Sharp transition of epitaxial film is obviously due to its high homogeneity. Similar picture is observed for the non-epitaxial films because this method is sensitive to the layers with the highest $T_c$. Fig. 2.10 illustrates that the top layer (c.a. 100 nm) of the (Nb,Ti)N film deposited on a glass wafer has the highest $T_c$ and competitive growth has reached a saturation in this layer. Thus this layer consists only of the grains with one orientation and a sharp transition is observed for this film as well.

2.5 Discharge and substrate - target distance selection

Fig. 2.14 illustrates the dependencies of the $T_c$, resistivity, and intrinsic stress on the

**Fig. 2.14.** $T_c$, film resistivity, and intrinsic stress of (Nb,Ti)N films deposited on glass wafers at ambient substrate temperature by DC- and RF-discharges.
total pressure for the (Nb,Ti)N films sputtered by 300 W DC and 200 W RF power on glass wafers. The N$_2$ flow rate is optimized at every pressure to achieve a maximum T$_c$. Thickness of all films is 500±20 nm. Deposition rate is 80±5 nm/min and 25±3 nm for DC and RF discharges correspondingly. T$_c$ and film resistivities have almost identical dependencies versus sputtering pressure for both of the discharges, while the intrinsic stress is much higher for the RF – sputtered films.

The influence of the substrate-target distance on the (Nb,Ti)N film properties is examined as well. Fig. 2.15 illustrates T$_c$, intrinsic stress, and resistivity versus sputtering pressure for the films deposited at 4 cm and 8 cm substrate-target distance. Nitrogen injection is optimized for every sputtering pressure to produce maximum T$_c$. All films on this plot are sputtered by 300 W DC power on glass substrates. All films are 500±20 nm thick. Deposition rate is 80±5 nm/min at for 8 cm substrate-target distance and 180±10 nm/min for 4 cm substrate-target distance. As seen from the Fig. 2.15 reduction of substrate-target distance is equivalent to a decrease in sputtering

![Graph showing T$_c$, film resistivity, and intrinsic stress vs. sputtering pressure.](image)

**Fig. 2.15.** T$_c$, film resistivity, and intrinsic stress of (Nb,Ti)N films deposited on glass wafers at different substrate-target distance.
pressure. This is an additional confirmation that the film properties are determined by thermalization, since the product of sputtering pressure and substrate-target distance determines the thermalization conditions [13]. In addition this experiment indicates that film properties do not depend on deposition rate, in contrast with the results published in ref. 14. Since there is no considerable difference between the films sputtered at different substrate-target distances, the maximum substrate-target distance is selected to achieve maximum film uniformity.

2.6 Conclusions

The properties of NbN, (Nb,Ti)N, and (Nb,Zr)N, deposited on glass and MgO wafers at ambient substrate temperature are compared. The best properties are observed for (Nb,Ti)N films sputtered from a NbTi alloy target with 30 at. % Ti. (Nb,Ti)N films deposited on Si, sapphire, and glass wafers show a considerable degradation of $T_c$ with film thickness due to poor crystallinity of the bottom layers of the films. Utilization of MgO wafers allows us to produce epitaxial (Nb,Ti)N and NbN films with improved properties and better homogeneity. While utilization of the RF-sputtered MgO under-layers results only in resistivity reduction. Both RF- and DC-discharges are producing films with similar $T_c$'s and resistivities. However DC discharge is selected for film deposition, because it produces films with lower compressive stress. Maximum substrate-target distance is selected for film sputtering because it provides the best uniformity and reduction of substrate-target distance does not improve the film properties.

References


Chapter 3

Properties of (Nb,Ti)N films

3.1 Introduction

Because the normal state resistivity of a conventional superconducting film provides a good estimate of RF losses in the film, this chapter is dedicated to a characterization of (Nb,Ti)N films, focusing in particular on this parameter. An understanding of the technological factors determining the film quality, combined with a detailed material study, will provide a platform for further improvement of the films and for predicting their behavior at THz frequencies. Various techniques are used for the deposition of nitrides, including DC and RF reactive sputtering, [1,2] ion-beam deposition, [3] reactive evaporation, [4] pulsed laser deposition, [5] and magnetron sputtering [6]. Because DC and RF magnetron sputtering are two of the most promising methods for device fabrication, this method is explored in this chapter.

In general, the properties of (Nb,Ti)N and similar materials like NbN or TiN show a strong dependence on the magnetron sputtering conditions. An increase in the substrate surface temperature by intentional heating, changing thermalization conditions of the sputtering yield by total sputtering pressure, or applying a substrate bias, results in a reduction of the resistivity, a change in the texture from (111) to (100), and a moderate increase in $T_c$ [7]. In this chapter the properties of the films sputtered under different total pressures are compared, focusing in particular on the strong dependence of film resistivity on sputtering pressure. Two different concepts have been proposed to explain the origin of high resistivities in carbides and nitrides of transition metals. Toth explains this effect by a high concentration and high degree of disorder of vacancies at both metal and nonmetal sites [8]. While Bacon et.al. state that the high resistivity of magnetron sputtered NbN films is due to voids on the grain boundaries [9]. In this chapter it will be shown that both mechanisms can play a role in determining the resistivity of (Nb,Ti)N films depending upon the sputtering conditions used.

3.2 Thornton diagrams and film growth

Film deposition may be modeled as a process consisting of four major steps [10].

1. The arriving atoms adsorb on the surface. This process can go in to different ways. The first one is typical for evaporation and CVD processes. The approaching molecule or
atom is trapped in so called physisorbed state on the surface by the van der Waals force. The particle in this state remains highly mobile except cryogenic temperatures. It may leave the surface after a while or turn into chemisorbed state, forming chemical bonds with the surface atoms. The second way of particle adsorption is typical for energy enhanced deposition like magnetron sputtering for instance. In this case the arriving particles have enough energy to adsorb directly into chemisorbed state. The mobility of adatom in the chemisorbed state is much lower compare to the chemisorbed state.

(2) Adatom diffuse a certain distance before incorporation into the film. The Arrhenius plot illustrated on the Fig. 3.1 describes the diffusion length of the adatom on the surface. Two branches of this curve correspond to burial and desorption regimes. The adatom in the desorption regime corresponds to high substrate temperatures when the adsorbed molecule or atom have enough energy to desorb or in the other words simply to evaporate from the film surface. The latter one corresponds to the case of relatively low temperatures when the adsorbate has enough time to find it’s place in the lattice of the growing film before the next layer of the film is deposited. The diffusion length of adatom in the burial regime is described by the following equation:

$$\Lambda = a \sqrt{\frac{V_s n}{J}} e^{-E_s/kT}$$

where $\Lambda$ is surface diffusion length, $a$ distance between the neighboring atoms on the film surface, $V_s$ is attempt frequency which depends on the substrate temperature and initial and final state of the particle. For example the attempt frequency of hopping between two physisorbed states can be much lower compare to the frequency of adsorbate moving from the chemisorption site to the physisorption site. $n$ – density of adsorption sites, $J$ is deposition flux, $E_s$ is activation energy for the surface diffusion, $k$ – Boltzman constant, $T$ - surface temperature. Surface diffusion exponentially increases with temperature and beening suppressed by increase in deposition rate. The surface diffusion in the desorption regime can be described by the following expression:

$$\Lambda = a \sqrt{\frac{V_s}{V_c}} e^{(E_c-E_s)/kT}$$

where $V_c$ desorption attempt frequency, $E_c$ – desorption activation energy.

In the case of magnetron sputtering and ambient substrate temperature the energy of

![Fig 3.1. Arrhenius curve: surface diffusion length versus substrate temperature.](image-url)
arriving atoms or molecules rather than substrate temperature determine surface diffusion. This is so called quenched growth. In this case the migration of adatoms is determined by the factors like local heating due to the "thermal spike" produced upon the impact, forward sputtering of the other atoms into the voids developed due to the lack of surface diffusion, higher "impact mobility" of the adatoms, etc. As it will be shown below, if the film growth conditions provide the longest possible $\lambda$, than the film will have the best crystallinity and very smooth surface.

(3) Initial aggregation of the film material, i.e. development of the chemical bonds between adatoms themselves and substrate surface and adatoms and sequential nucleation. Since the thick films are studied in this chapter, which appear to be continuos, this step of film growth will be discussed briefly. Three primary modes of film growth are well recognized up to now (Table. 3.2). Frank-van der Merwe or two-dimensional layer-by-layer growth occurs when the binding between the substrate and the film atoms is greater or equal than that between film atoms. The opposite situation results in the Volmer-Weber or 3-D Island growth. The third growth mode, often referred as Stranski-Krastanov, is a combination of the first two. In this case, after the formation of the first one or two monolayers the growth mode switches form 2-D layer-by-layer to 3-D island growth. Inspite of frequent observation of this growth mode in different systems, the reason of this transition is not very well understood by now.

Table 3.2. Schematic representation of three film growth modes.

<table>
<thead>
<tr>
<th>Growth mechanism</th>
<th>Less than one monolayer</th>
<th>Between one and two monolayers</th>
<th>More than two monolayers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frank-van der Merwe (layer by layer)</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>Volmer-Weber (3-D Island)</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>Stranski-Krastanov</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

(4) Development of the bulk film structure, i.e. roughness and crystallography. Movchan and Demchishin were the first to systemize the structure of the films grown by PVD [11]. Further this approach was studied and broadened by Thornton [12]. Different modifications of structural-zone diagram (SZD) have been proposed by different authors up to now. The film properties correlate with different technological factors such as the substrate temperature, gas pressure, ion assistance, deposition rate, etc. However since all these factors determine $\Lambda$ (the key parameter of film growth), the famous Thornton SZD is plotted on Fig. 3.2 versus $\Lambda$. Z1 structural zone occurs when surface diffusion of adatoms is almost suppressed; that is $\Lambda<a$. Z1 consists of columns with poor crystallinity typically tens of nm in diameter separated by voids a few nm across. ZT occurs when $\Lambda$ is higher than in the case of Z1 but still $\Lambda<\lambda$. Film structure is similar to the Z1 zone, but the
voids are absent. Z2 occurs when $A > a$. The film consists of grains having better crystallinity compare to the previously described structural zones. The grains have tight grain boundaries and stretching throughout the film thickness as usual. The surface of these grains is often faceted. Z3 occurs when $A > a$. Grains have excellent crystallinity and equiaxed shapes. The surface is much smoother compare to the other structural zones, however grain boundaries can develop grooves. The boundaries between these structural zones are rather smeared. The growth mode can change throughout the film thickness. For instance film structure may change with film thickness from ZT to Z2. Z1 and ZT structural zones correspond to “quenched growth” process in which the adatom is immobilized almost at the place where it lands.

Intrinsic stress of the films produced by magnetron sputtering has strong dependence on sputtering pressure and correlates with SZD (Fig. 3.3) [14]. At high pressures when the particles of the sputtering yield are thermalized the film is growing in the quenched

![Graph](image)

**Fig. 3.3.** Schematic behavior of film stress versus gas pressure during magnetron sputtering.
regime with multiple voids on the grain boundaries. Film structure corresponds to Z1 structural zone. As the pressure decreases the arriving adatoms are less thermalized and therefore more mobile. The voids between the grain boundaries start to collapse and the tensile stress starts to build. The film structure switches towards ZT. Further reduction of sputtering pressure leads to an increase in fast neutral bombardment of the film surface and even higher adatom mobility. As a result Ar atoms incorporated in the lattice case compressive stress and film structure turns into Z2 zone.

3.3 Experimental

Films of (Nb,Ti)N are deposited by reactive magnetron sputtering in a Nordiko-2000 sputtering system with a base pressure of 4·10⁻⁵ Pa. This sputtering machine is equipped with a cryopump and a throttling valve, which together determine the process pressure, while the injection of Ar and N₂ gases is controlled by flow-meters. In order to avoid the hysteretic sputtering regime, the pumping rate is fixed at a high value of 750 l/s for all experiments [15]. A 99.8% pure alloy target with 30 at. % Ti and 70 at. % Nb is used. All films are sputtered with 300 W DC power, resulting in a deposition rate of 80 ± 5 nm/min. Wafers are fixed to the copper chuck with diffusion pump oil to stabilize the thermodynamics of growth. In order to maximize film uniformity, the substrate-target distance is set to the maximum for this sputtering system, 8 cm.

Films (160±10 nm thick) sputtered on silicon wafers were used for T₀, resistivity, XRD, room temperature Hall coefficients, density, and intrinsic stress measurements. The stress in the films is evaluated measuring the deflection of the wafer before and after film deposition with a profilometer. The stress value is calculated with the help of Stoney’s equation [16], using a Young’s modulus and Poisson’s ratio for (100) Si taken from ref. [17]. T₀ is evaluated from the dependence of film resistivity on temperature. Film density is determined from the weight of the layer. The Hall coefficient is measured using standard Hall voltage measurement.

The chemical composition of the films is measured by Rutherford Back Scattering spectroscopy (RBS) using 1 MeV He⁺ beam for sample irradiation. The back-scattered particles are detected at an angle of 165°, and the measurements are done in a UHV chamber with a base pressure of 5·10⁻⁶ Pa. A “random” RBS spectrum is obtained by summing up the RBS spectra acquired during a 360° RBS azimuthal scan measurements with a 10° beam incidence off the surface normal. A detailed analysis of the measured RBS spectra is performed by the “RUMP” program [18]. Relatively thin films (50 nm) sputtered on Si wafers are used for this kind of analysis in order to allow the scaling onto the substrate yield in the RBS simulation routine. It is expected that the nitrogen content does not depend on the film thickness, because the chemical composition is determined by the nitration of the cathode, rather than by processes taking place on the film surface [19]. Thus, the RBS data on the chemical composition of the thin films should be valid also for thicker samples. Note that RBS also revealed that the level of possible contaminants (such as oxygen and carbon) in all films is below 1 at. %.

XRD Θ-2Θ scans in the 2Θ range from 20° to 125° are performed using a Rigaku D/max-Rc diffractometer equipped with a 12 kW X-ray generator of Cu Kα radiation and a graphite crystal-monochromator. X-Ray diffraction texture measurements are performed with a Bruker- AXS D5005 diffractometer equipped with a Huber Eulerian Cradle, also using Cu Kα radiation. Ψ- scan technique is performed, using the following
setings. The specimen tilt-angle (ψ) range is 0° - 80° with a step size of 10°. 2θ range was selected from 32° to 45° to monitor to most intensive [111] and [200] reflections. Integral reflection intensity, corrected for diffraction volume factor of cos(ψ), is used for the texture analysis. Plan-view samples are prepared by a standard technique - mechanical thinning down to 30 μm and followed by ion milling using a Gatan 600 Duo Ion Mill. The specimens are examined with a Philips EM430ST transmission electron microscope operated at 200kV.

3.4 Results and discussion

Nitrogen injection has been optimized for the wide range of total sputtering pressures in order to have maximum Tc of the (Nb,Ti)N films. The limits of the pressure range are determined by film degradation caused by destructive bombardment of the growing film by the fast neutrals at low pressures and high thermalization conditions at high pressures [20]. Fig. 3.4 and Fig. 3.5 illustrate the dependence of film properties versus total sputtering pressure. Tc and the Hall coefficient are weakly dependent on pressure, film resistivity increases strongly while compressive stress decreases strongly with increasing pressure. Film density decreases with increasing pressure. The chemical composition is almost stoichiometric. The ratio on nitrogen to metal atomic concentration for all films is in the interval of 1.02±0.02. The ratio of Nb and Ti in the films is almost the same as in the target.

Two separate structural zones of the (Nb,Ti)N films versus sputtering pressure can be identified according to Thornton classification. Films sputtered in the pressure range of 5-9 mTorr belong to the ZT structural zone, since they are in a state of compressive stress and XRD analysis shows numerous peaks in the θ-2θ scans, i.e. there is no strong texture present (Table 3.2). A further increase in the sputtering pressure results in a flattening of the stress curve at ≈ 0 GPa. This allows to attribute the films sputtered in the pressure range of 10-12 mTorr to the Z1 structural zone. According to Thornton films in the ZT structural zone have tight grain boundaries, while the films in the Z1 structural zone have voids on the grain boundaries. Those results are in good correlation with the data obtained by the TEM. Fig. 3.6 illustrates several plan-views of the films sputtered under different pressures. Only the film belonging to Z1 structural zone have white regions at the grain boundaries, which could be voids or thick layers of amorphous material, while all other films shown on the Fig. 3.6 have tight grain boundaries.

Since low-resistivity films are needed for SIS mixers films belonging to the ZT structural zone will be discussed further. In particular, noting that the measured Tc and Hall coefficient have a relatively moderate dependence on sputtering pressure, when compared with the change in resistivity, it is concluded that the variation of the resistivity is not determined by changes in the density-of-states at the Fermi level. Furthermore observation of a steady nitrogen concentration (slightly exceeding 50 at. %) and the increase in film-density with the decrease of sputtering pressure gives us a clear indication that there is a variation in the quenched-in vacancy concentration in the films. Because the sputtering pressure controls the heat-flux towards the substrate by the thermalization of fast neutrals and the particles of the sputtering yield, this increase in the vacancy concentration is associated with a reduction of surface diffusion as the sputtering pressure increases [21].
**Fig. 3.4.** *Transition temperature, film resistivity, and intrinsic stress of (Nb,Ti)N films deposited under different pressures.*

Since increase of conductivity and compressive stress are in good correlation in the ZT structural zone, it is interesting to discuss an alternative mechanism for the observed vacancy concentration variation. In particular annealing of TiO samples under pressures $= 0.01$ GPa results in a considerable reduction of the vacancy concentration [22]. During magnetron sputtering similar conditions for the film layers close to the surface of the film can take place. High temperature is produced by plasma heating and high pressure is created by intrinsic stress in the (Nb,Ti)N film. However, the experiments show that the intrinsic stress in the films also depends on film thickness, while film resistivity is determined exclusively by pressure. Thus, it is concluded that intrinsic stress has a minimal effect on film resistivity, and that film resistivity is determined exclusively by the thermalization conditions in the glow discharge.
Fig. 3.5. Hall coefficients and density of (Nb,Ti)N films sputtered under different pressures.

Table 3.2. Θ-2Θ XRD patterns of the (Nb,Ti)N films sputtered under different total pressures. Top peak intensities are illustrated in this table.

<table>
<thead>
<tr>
<th>Sputtering pressure</th>
<th>hkl</th>
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<tbody>
<tr>
<td>mTorr</td>
<td>111</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
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<td>7</td>
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<td>100</td>
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<tr>
<td>11</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
</tr>
</tbody>
</table>
Fig. 3.6. To be continued on the next page.
Fig. 3.6. Plan view TEM images of (Nb,Ti)N films deposited under sputtering pressures (5, 7, 9, and 12 mTorr) pictures A-D correspondingly.
High vacancy concentration and high degree of disorder can modify the X-Ray scattering amplitudes and, as a consequence, change the XRD reflections intensity. In order to determine the significance of this effect Ψ-scans for films sputtered under pressures of 6 and 9 mTorr are performed (Fig. 3.7). Data analysis showed that the film sputtered under 6 mTorr pressure has a weak (100) texture, while the film sputtered under 9 mTorr pressure is has a distinct (111) texture. The increase of [111] peak intensity at 50° for the sample sputtered under 6 mTorr pressure is due to the fact that the angle between (111) and (200) planes is 54.7° in fcc lattice. Similar mechanism leads to an increase in 200 peak intensity at the tilt angle of 50° for the sample sputtered under 9 mTorr pressure. Since the angle between {111} equivalent planes is 70.4° an increase of 111 integral peak intensity at 70° is observed for the film sputtered under 9 mTorr. Thus, the observed changes of the X-Ray patterns summarized in the Table 3.2, are mainly due to different textures present in the films. Similar changes in texture as a result of intentional heating were previously observed for TiN films [23]. Moreover, the artificial initiation of (100) texture by sputtering on a MgO underlayer results in a reduction of resistivity and slight increase of Tc in NbN films [24]. These results are in good correlation with the observations, since in this case the same changes in texture (from (111) to (100)) are initiated by reducing the sputtering pressure to elevate the substrate surface temperature.

Fig. 3.7. Integral peak intensity for Θ-2Θ scans at different tilt angles. The upper (bottom) plot corresponds to the film sputtered under 6 mTorr (9 mTorr) pressure.
3.5 Conclusions

The structural and electrical properties of (Nb,Ti)N films are examined over a wide range of sputtering pressures. TEM analysis revealed that the films consist of 20-40 nm grains. Films sputtered under low pressures have a weak (100) texture, while films sputtered under high pressures have a distinct (111) texture. A change of the film structure from the Z1 structural zone to the ZT structural zone is observed as the sputtering pressure decreases. Tc has a moderate dependence on the sputtering pressure, while film resistivity increases one order of magnitude as the pressure increases. Because all of the films have RRR resistance ratios in the vicinity of unity, it is concluded that the origin of high resistivities is related to crystal imperfections. In particular, film resistivity is determined by vacancies in the ZT structural zone, while the voids on the grain boundaries and vacancies together determine the resistivity in the Z1 structural zone.

References

Chapter 4

Comparison of balanced and unbalanced sputtering sources

4.1 Major energy beams in magnetron sputtering systems

Magnetron sputtering is one of the most widely used techniques for thin film deposition. Over the last 30 years, this method has become a well-studied subject. This technique has a lot of remarkable advantages over other techniques: any material can be volatized by sputtering, deposition rate can be made uniform over large areas, and compounds are volatized stoichiometrically. Glow discharge plasma, confined by magnetic trap, is used for the sputtering of target material (Fig. 4.1). The crosswise magnetic field over the cathode traps the beam electrons in orbits and thus greatly increases their path length before they finally escape to the anode by collisional scattering. This allows to operate the magnetron sputtering source at much lower

![Diagram of magnetron sputtering](image)

**Fig. 4.1.** Cross-sectional view of the balanced RPK-125 magnetron and magnetic field for new and eroded targets. The eroded target profile is indicated by shading.
pressures, compared to diode sputtering. Less than a few percent of the electrical energy supplied to the system is used to eject sputtered atoms and secondary electrons. The remainder of the energy appears as heat; about three quarters of the heat is adsorbed by the target and most of the rest is adsorbed by the substrate [1]. There are four major energy fluxes towards the substrate in this process: particles of the sputtering yield, fast neutrals, ions, and secondary electrons.

The most energetic and the most important flux is the flux of the sputtered cathode particles. The typical energy of the sputtering yield particles is a few eV. Sputtered particles have Thompson distribution over energy with a threshold order of a binding energy [2]. The angular distribution is generally assumed to vary as $\cos(\Theta)$, where $\Theta=0^\circ$ corresponds to a direction perpendicular to a substrate surface. Since the energy of sputtered particles is much higher compared to a temperature of sputtering gas particles, thermalization conditions of the sputtering yield are very important for the formation of the film structure. Moreover, this flux is causing considerable gas rarefaction in front of the sputtering source. The sputtering rate in magnetron systems is proportional to a product of a discharge current and a sputtering yield coefficient. In most of the cases DC magnetron sputtering systems operate in a relatively narrow interval of voltages, where sputtering yield coefficient is simply proportional to the discharge voltage. Therefore sputtering rate is proportional to the power applied to a target [3].

A small fraction of ions bombarding the cathode surface are neutralized upon the impact and reflected with a retaining of a substantial fraction of initial energy [4]. These, so called, “fast neutrals” are forming the second energy beam. This flux transfers much less energy compared to the previously discussed one. However, since the energy of fast neutrals is higher than the threshold of incorporation (=10 eV), this flux determines the argon peening into film matrix. The argon peening is one of the major factors determining the compressive stress in the films. This process is described by the following equation:

$$\sigma_{x,y} = B \left( \frac{Y}{1-\nu} \right) \frac{J_i N_i}{J_r}$$

where $B$ - proportionality constant, $Y$ - Young's modulus, $\nu$ Poisson's ratio, $J_i$ - ion flux or the flux of fast neutrals bombarding the surface of the growing film, $N_i$ number of interstitials produced per bombarding ion, $J_r$ - deposition flux. In general the process of stress formation in thin films is a superposition of various effects. The stress may change even a sign throughout the thickness of the film grown under static conditions. However the control of the atomic peening, caused by the flux of fast neutrals, is a sufficient tool for mastering of the film stress in sputter-deposited films [5]. Fig. 4.2 illustrates an excellent correlation between the incorporated argon and intrinsic stress in Nb films. Utilization of noble gases of more heavy atoms compare to Ar allows to reduce the atomic peening [6].

If the substrate is located in the plasma bulk layer, the interaction of the plasma with the substrate surface results in two additional heat fluxes towards the substrate, i.e. bombardment by secondary electrons and ion assistance. This can be achieved by location of the substrate close to the sputtering source for a conventional balanced configuration. The alternative way is the utilization of an unbalanced sputtering source (Fig. 4.3). The outer magnetic ring is made stronger compare the balanced design in this case, therefore secondary electrons are guided by the magnetic field lines towards the substrate. This plasma heating is different for the grounded and “floating” wafers. If the
**Fig. 4.2.**  Ar content in Nb films versus film stress. Small numbers besides the plots show Ar pressure during sputtering in Pascals. (Modified from ref 5).

**Fig. 4.3.**  Cross-sectional view of the homemade unbalanced magnetron and magnetic field for new and eroded targets. The eroded target profile is indicated by shading.
substrate is “floating” than the ions are accelerated towards the substrate and electrons are repelled by the “self-bias” potential [7]. For Maxwellian distribution of electrons in plasma the “self-bias” potential is determined by the following equation: \( \Delta V_f = -T_e \ln(m_e/2.3m_i) \), where \( T_e \) is electron temperature, \( m_e \) and \( m_i \) are the weights of electrons and positive ions in the plasma. In the case of DC sputtering the presence of a net current makes plasma potential very low. Therefore if the wafer is grounded then the very low plasma potential is not able to repel the electrons or to accelerate significantly the ions [7]. Therefore in this case, only the electrons mainly cause the substrate heating in this case.

4.2. Reactive sputtering

Reactive magnetron sputtering is widely used for the production of nitrogen, oxygen, or carbon containing compounds [8]. Compound deposition by the reactive sputtering from a metal target generally lowers target fabrication cost and increases target purity as compared to using a compound target, but it complicates process control when film composition is critical. The concentration of reactive gas in the reactor determines the concentration of the elements, mentioned above, in a film. The ionized molecules of reactive gas are accelerated towards the cathode by the potential of the cathode sheath. This bombardment results in a target poisoning, which is determined by the balance between the flux of reactive ions, responsible for the formation of the compound, and the flux of Ar ions sputtering the target material. The main problem of the reactive sputtering is the hysteresis loop (Fig. 4.4). Sputtering source works like a getter pump with respect to a reactive gas. Sputtering rate and reactive gas consumption go down with increase in reactive gas injection. Moving along the forward branch on the Fig. 4.4, results in a positive feed back at a certain point and rapid transition of the target into completely poisoned state. Indeed, increase in reactive gas partial pressure leads to a reduction in sputtering rate and less reactive gas consumption or in the other words higher partial pressure of reactive gas. Similar “mirrored” process occurs on the return branch of curve illustrated on the Fig. 4.4. The sharp rise in sputtering rate occurs at lower injection of reactive gas, because the system has a “memory”, or in the other words the cathode remains in the completely poisoned state at lower injection rates of

![Diagram](image-url)

**Fig. 4.4.** Typical process behavior of metal sputtering in a reactive gas.
reactive gas, compare to the forward branch. It is very difficult to operate the system in
the region of hysteresis, since it tends to slide from the forward branch to the return
branch in this region. Using high pumping rate can eliminate this problem. In this case
the fluctuations of reactive gas partial pressure caused by getter pumping are negligible.
Non-hysteretic regime can be easily achieved in a laboratory sputtering system with
small sputtering sources, while in industrial machines equipped with big sputtering
sources (where the getter pumping is compatible to the pumping rate) the hysteretic
regime is inevitable. All vacuum systems, used in experimental work described in
this thesis, are operated in non-hysteretic regime because of one more clear advantage. The
sputtering rate in magnetron system depends on two key parameters, like applied power
and target material. Therefore film stoichiometry can be controlled in a straightforward
way, as ratio of film deposition with and without nitrogen injection. Thus it is necessary
to employ chemical analysis technique only once to measure this ratio, since it does not
depend on sputtering pressure or applied power.

4.3. Debut idea

A wide range of important aspects have been identified and independently studied
including the current-voltage relations in magnetrons [9], the pressure-dependence of the
stress in the sputtered films [10], effects related to the flux of fast neutrals [11], gas
rarefaction in front of the target due to the directed “wind” of sputtered particles [9],
plastic flow produced by stress [12], the formation of the compound layers on the target
surface during reactive sputtering [13], and different configurations of magnetic traps
[14]. In this chapter an opposite approach is followed. The analysis of the properties of
deposited films is used to evaluate the performance of the sputtering source.

The origin idea of this approach was suggested by the publication of Imamura et al
[5]. Fig. 4.5 illustrates the classical dependence of the intrinsic stress of Nb films versus
sputtering pressure for different discharge currents. The position of a process on this
curve determines the Nb film properties, in agreement with Thornton classification of
structural zones [15]. All these intrinsic stress points fit the same curve if plotted versus
the discharge voltage (Fig. 4.6). Imamura et al. suggest the following explanation: “The
Nb target’s surface is sputtered by the accelerated Ar+ ions. If the energy exchange

![Fig. 4.5. Nb film stress versus Ar pressure (modified from ref. 5).](image-url)
between Ar⁺ ion and Nb occurs without any energy loss, the kinetic energy of the Nb particles ejected from the target equals that of the incident Ar⁺ ions. Since the bombardment of deposited Nb particles causes compressive stress, we assume that the Nb film stress is strongly related to the cathode voltage [5]." This explanation is in clear contradiction with the well-known fact that the energy of sputtered particles is approximately equal the binding energy (several eV) [2], while the energy of the bombarding Ar⁺ ions is several hundred eV. An other explanation can be proposed on the basics of the work of Rossnagel et al [9]. They have shown that considerable gas rarefaction occurs in front of the target during sputtering [9]. This effective gas density controls two processes: a) the thermalization conditions for the sputtering yield and fast neutrals, and b) the electron temperature in the plasma bulk layer of the glow discharge. Since the discharge voltage, \( V \), is determined by the following equation \( V = \alpha (kT_e)^{0.5} \) (where \( \alpha \) is a constant for a given target-gas combination, \( k \) is the Boltzman constant, and \( T_e \) is the electron temperature), it is concluded that this value is indicative of the effective pressure between the cathode and the substrate. On the basis of these considerations, the concept of the approach is formulated: a) thermalization is the main technological factor determining the properties of films deposited at ambient substrate temperature (in the other words, if the wafers are heat-sunk to the chucks maintained at room temperature, a classical case of quenched growth takes place [16]), b) monitoring the dependence of the intrinsic stress on sputtering pressure provides sufficient information for general sputtering source characterization.

### 4.4. Experimental procedure

Films of (Nb,Ti)N are deposited by dc-magnetron sputtering in a Nordiko-2000 sputtering system with a base pressure of 4×10⁻⁵ Pa. This machine is equipped with a cryopump and a throttling valve, which together determine the process pressure, while the injection of Ar and N₂ gases is controlled by flow-meters. In order to avoid the hysteretic sputtering regime, the pumping rate is fixed at a high value of 750 l/s for all experiments [17]. An alloy target with 30 at.% Ti and 70 at.% Nb is used. In order to
maximize film uniformity, the substrate-target distance is set to the maximum for our sputtering system, 8 cm.

A homemade unbalanced 75 mm magnetron sputtering source is used for the deposition of (Nb,Ti)N (Fig. 4.3). The outer ring of a Leybold PK-75 magnet set is doubled to obtain an unbalanced magnetic trap and a magnetic lens is used to partially loop the magnetic field lines. The purpose of the magnetic lens will be discussed in more detail below. A balanced version of this sputtering source is obtained by replacing the magnetic lens with an additional central magnet from the PK-75 magnet set. The rectangular component of the magnetic field above the center of the outer magnet ring is 351 Gauss for both configurations. The perpendicular component of the magnetic field in the center of central magnet is 577 Gauss for the balanced design and 254 Gauss for the unbalanced one.

NbN films are deposited in a Leybold high vacuum system L-560 UV using a RPK-125 dc sputtering source at a base pressure of $5 \times 10^{-5}$ Pa. This sputtering system is not equipped with a throttling valve, so the partial pressure of the process gases is controlled by flow meters. The pumping speed of 1000 l/s, provided by the TMP pump, results in the non-hysteretic sputtering regime. The substrate-target distance is 7 cm.

All films (260±10 nm thick) are sputtered on glass wafers. The substrates are fixed with diffusion pump oil to a copper chuck, which is maintained at 10°C to stabilize the substrate temperature. The stress in the (Nb,Ti)N films is evaluated by measuring the deflection of the wafer before and after film deposition with a profilometer. The stress value was calculated with the help of the Stoney’s equation [18], using a Young’s modulus and Poisson’s ratio taken from ref. 19. The intrinsic stress in the NbN films is estimated from the curvature of 0.2 mm thick glass strips, as measured by an interference microscope [20]. $T_c$ is evaluated from the dependence of film resistivity on temperature. The dc film resistivity is measured at 20 K, since this value is related to the RF-losses in a microwave tuning circuit. Measuring the resistivity at 20 K instead of 300 K is also more informative from the prospective of the quenched-in crystal point defects concentration. XRD Θ-2Θ scans in a 2Θ range from 34° to 43° are performed using a Rigaku D/max-Rc diffractometer equipped with a 12 kW X-ray generator of Cu Kα radiation and a graphite crystal–monochromator.

4.5. Comparison of balanced and unbalanced sputtering sources

In order to evaluate the effectiveness of the balanced and unbalanced magnetic traps of our home-made sputtering source, the properties of the glow discharge for the two configurations at 6 mTorr Ar pressure are compared. The self-bias of the floating substrate table is -19 V for the unbalanced configuration and -5 V for the balanced case. Furthermore, the ionic current measured with a -30 V biased substrate table is 60 mA for the unbalanced configuration and 7 mA for the balanced case. Finally, the grounding current is equal to the discharge current ($\approx -1$ A) for the unbalanced configuration, while it is equal to -10 mA for the balanced configuration. These results show that, as expected, the magnetic trap in the balanced configuration is much more effective than in the unbalanced configuration.

The properties of (Nb,Ti)N films obtained using the balanced and unbalanced magnetron configurations are shown on Fig. 4.7. All films are sputtered under 300 W applied power on a “floating” substrate table, and the nitrogen flow rate is optimized to
obtain the highest $T_c$ for each total pressure. This optimization of the nitrogen injection results in the same deposition rate for each data point (80±10nm), because the poisoning of the target determines both the chemical composition of the films (stoichiometric films have the maximum $T_c$) and the sputtering rate. It is interesting to mention that optimum nitrogen injection is the same for balanced and unbalanced configurations. In the other words this parameter does not depend on configuration of the magnetic trap. For both sources, reducing the total sputtering pressure leads to a slight increase in $T_c$ and a decrease in resistivity. This is attributed to a reduced thermalization of the sputtering yield and increased film bombardment by fast neutrals. At the lowest pressures used (4-5 mTorr), this bombardment becomes strong enough to damage the growing film, resulting in a saturation of the resistivity at $\approx 90\ \mu\Omega\cdot\text{cm}$ and a degradation of $T_c$. As is seen in Fig. 4.7, the properties of (Nb, Ti)N films obtained with the unbalanced
configuration are similar to those of films obtained with the balanced configuration at lower total pressures. This indicates that the effect of the ion bombardment generated by the unbalanced source is similar to the effect of the increased fast neutral bombardment obtained by reducing the sputtering pressure. Grounding of the wafer during sputtering with the unbalanced source (hereby suppressing the ion bombardment and enhancing the secondary electron heating of the wafer), is also equivalent to increasing of the sputtering pressure, in terms of its effect on film properties. This indicates that electron heating of the substrate has significantly less effect on the properties of the growing film than ion bombardment.

4.6. Performance of the balanced sputtering source versus target erosion

The behavior of the Leybold dc-sputtering source RPK-125 (seen in Fig. 4.1) is investigated versus target erosion. NbN films are sputtered with DC power from 10% and 90% eroded 8 mm thick Nb target. Independent of target erosion, the self-bias of the “floating” table is less than 1 V, indicating that the RPK-125 sputtering source has a balanced and very effective magnetic trap. Ar and N₂ flow rates are optimized for three different values of applied power to produce stress free films from a fresh target with maximum Tₑ (samples A₁, B₁, C₁ in the Table 4.1). The resulting deposition rate and nitrogen injection are proportional to the applied power. Optimum deposition conditions for all these films correspond to the same deposition rate ratio of Nb and NbN, indicating identical chemical composition. Since the stress in the films is determined by effective gas concentration in between the substrate and the sputtering source, the pressure has to be slightly reduced with reduction of applied power to correct for a reduction of gas rarefaction caused by hot particles of a sputtering yield.

The process of target erosion results in the formation of a very curved trench on the cathode surface (Fig. 4.1). This leads to two different events. First, the sputtering rate goes down due to a sputtering of a target material from one side of the erosion trench and subsequent condensation on the other side. As a result the optimum nitrogen injection has to be reduced about 30% to produce the films with highest Tₑ (samples A₂, B₂, C₂). An acceptable approach for the optimum Tₑ maintenance throughout the target life time is monitoring the ratio of NbN and Nb deposition rate. As seen from Table 4.1 this parameter does not depend on the applied power and target state. Second, the process of the target erosion results in an increase in sputtering yield thermalisation, because a majority of the sputtered particles leaves the grooved target at certain angle with respect to the vertical direction. Therefore the particles of the sputtering yield will undergo more collisions before reaching the substrate in this case. More over reduction in sputtering rate causes lower gas rarefaction. This increase in sputtering yield thermalisation results in increase in NbN film resistivity and decrease in [200] and [111] XRD peaks ratio. Therefore it is concluded, that the process of target erosion is equivalent to an increase in substrate-target distance or gas pressure.

In addition, films sputtered from eroded target without nitrogen injection correction (samples A₃, B₃, C₃), show much higher resistivities and lower ratios of [200] and [111] XRD peaks intensities. The process of target erosion results in a considerable change of the beam pattern of the sputtering yield, that the tooling factor of the quartz crystal thickness monitor has to be corrected through-out the target life-time.
Table 4.1. Optimum sputtering conditions (nitrogen, argon injection, ant total pressure), deposition rates, ratio of deposition rates of NbN and Nb, and film properties (transition temperature, film resistivity, RRR, ratio of [200] and [111] XRD peaks) for different applied powers and target states. Samples A2, B2, C2 are sputtered with corrected nitrogen injection to produce maximum transition temperature. Samples A3, B3, C3 are sputtered under the same sputtering conditions as samples A1, B1, C1 correspondingly.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target state</td>
<td>fresh</td>
<td>eroded</td>
<td>eroded</td>
<td>fresh</td>
<td>eroded</td>
<td>eroded</td>
</tr>
<tr>
<td>Power, W</td>
<td>800</td>
<td>800</td>
<td>800</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Ar, sccm</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>130</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>N₂, sccm</td>
<td>19</td>
<td>15</td>
<td>19</td>
<td>14</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>Total pressure, mTorr</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>NbN deposition rate, nm/min</td>
<td>120</td>
<td>96</td>
<td>80</td>
<td>90</td>
<td>66</td>
<td>55</td>
</tr>
<tr>
<td>Ratio of NbN and Nb deposition rates</td>
<td>0.61</td>
<td>0.63</td>
<td>0.52</td>
<td>0.62</td>
<td>0.64</td>
<td>0.53</td>
</tr>
<tr>
<td>Tₛ, K</td>
<td>14.5</td>
<td>14.6</td>
<td>13.7</td>
<td>14.6</td>
<td>14.4</td>
<td>13.5</td>
</tr>
<tr>
<td>R₂₀K, µΩ·cm</td>
<td>164</td>
<td>206</td>
<td>233</td>
<td>164</td>
<td>208</td>
<td>250</td>
</tr>
<tr>
<td>RRR</td>
<td>0.91</td>
<td>0.88</td>
<td>0.84</td>
<td>0.91</td>
<td>0.88</td>
<td>0.82</td>
</tr>
<tr>
<td>I[200]/I[111]</td>
<td>1.1</td>
<td>0.78</td>
<td>0.6</td>
<td>1.0</td>
<td>0.77</td>
<td>0.62</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample number</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target state</td>
<td>fresh</td>
<td>eroded</td>
<td>eroded</td>
</tr>
<tr>
<td>Power, W</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Ar, sccm</td>
<td>110</td>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>N₂, sccm</td>
<td>10</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Total pressure, mTorr</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>NbN deposition rate, nm/min</td>
<td>60</td>
<td>42</td>
<td>35</td>
</tr>
<tr>
<td>Ratio of NbN and Nb deposition rates</td>
<td>0.61</td>
<td>0.63</td>
<td>0.52</td>
</tr>
<tr>
<td>Tₛ, K</td>
<td>14.7</td>
<td>14.7</td>
<td>13.8</td>
</tr>
<tr>
<td>R₂₀K, µΩ·cm</td>
<td>167</td>
<td>210</td>
<td>257</td>
</tr>
<tr>
<td>RRR</td>
<td>0.91</td>
<td>0.88</td>
<td>0.8</td>
</tr>
<tr>
<td>I[200]/I[111]</td>
<td>1.05</td>
<td>0.72</td>
<td>0.6</td>
</tr>
</tbody>
</table>

4.7. Performance of the unbalanced sputtering source versus target erosion

The behavior of the unbalanced sputtering source versus target lifetime is examined as well. Taking into account the results of the previous section, the magnetic lens is used to stretch and flatten the erosion track. As a result, it is necessary to correct the nitrogen injection less than 10% for sputtering form 10%- and 90%-eroded 5 mm thick targets.
An examination of the properties of the glow discharge at 6 mTorr Ar pressure shows that the self-biasing of the substrate table is -19 V for the fresh target and -22 V for the grooved one. Additionally, the ionic current measured with a -30 V biased substrate table is 60 mA for the new target and 82 mA for the grooved one. These changes can be attributed to a decrease in the effectiveness of the magnetic trap through the target lifetime, due to the magnetic field produced by the outer ring becoming stronger as the target becomes grooved (see Fig. 3), making the magnetic trap more unbalanced.

The properties of the (Nb,Ti)N films obtained from the fresh and eroded targets are illustrated in Fig. 4.8. From this figure, it is seen that there is a significant increase in the conductivity and intrinsic stress of (Nb,Ti)N films deposited from the grooved target, relative to those deposited from a fresh target. Furthermore, at the lowest pressures (4-5 mTorr) the substrate bombardment actually becomes strong enough to cause a plastic flow of films sputtered from the grooved target (seen from the flattening of the stress

![Graph showing Tc, K, film resistivity, and film stress over sputtering pressure.]

**Fig. 4.8.** $T_c$, intrinsic stress, and film resistivity of (Nb,Ti)N films obtained from the fresh and eroded targets using the unbalanced sputtering source and a "floating" substrate.
curve in Fig. 4.8). These results are in direct contrast to the decrease in conductivity and intrinsic stress observed previously for NbN deposition using a balanced sputtering source. This can be explained by a significant increase in the ion bombardment of the substrate due to the previously discussed reduction in the effectiveness of unbalanced magnetic trap. This effect is insufficiently compensated by the increased thermalization of the sputtering yield and reduced fast neutral bombardment expected to result from the target becoming grooved. Thus, from Fig. 4.8, it is concluded that the process of target erosion for the unbalanced sputtering source is equivalent to a sputtering pressure decrease.

In order to suppress the contribution of ionic bombardment, this experiment is repeated with a grounded substrate table. As is seen from a comparison of Fig. 4.8 and Fig. 4.9, this results in less-stressed films at low pressures and a smaller deviation of film

![Graph](image)

**Fig. 4.9.** $T_c$, intrinsic stress, and film resistivity of (Nb,Ti)N films obtained from the fresh and eroded targets using the unbalanced sputtering source and a grounded substrate.
properties throughout the target lifetime. XRD does not show any considerable differences in the film texture for the films sputtered under the same pressure from the fresh and grooved targets (Fig. 4.10). Furthermore, it is seen that it is possible to select an operating point at 5 mTorr, for which the film properties are roughly independent of the target erosion state and satisfy the conditions for device production. At this point, the films have stress $\approx -2$ GPa, $T_C \approx 14.3$ K, and resistivity $= 100 \mu \Omega \cdot \text{cm}$.  

![Graph](image)

Fig. 4.10. Ratio of [100] and [111] XRD peak intensities of (Nb,Ti)N films obtained from the fresh and eroded targets using the unbalanced sputtering source and a grounded substrate.

### 4.8 Conclusions

The balanced and unbalanced sputtering sources are characterized and compared by monitoring the dependence of intrinsic stress on sputtering pressure. This curve is used because it can be directly related to the other film properties using the Thornton classification. Following this approach, it is found that no significant difference between the balanced and unbalanced sputtering sources, since the properties of the (Nb,Ti)N obtained from unbalanced sputtering source are equivalent to the properties of the (Nb,Ti)N films obtained from the balanced one under lower sputtering pressures.

An evaluation of the NbN and (Nb,Ti)N film properties leads us to a conclusion that the heat flux towards the substrate is not stable throughout the target lifetime. The unbalanced sputtering source shows a change in (Nb,Ti)N film properties equivalent to a decrease in the sputtering pressure, while the balanced sputtering source shows the opposite behavior. Furthermore, using an unbalanced source together with a grounded substrate table, it is possible to choose deposition conditions which yield stable and reproducible (Nb,Ti)N film properties throughout the target lifetime.

This approach of monitoring the film intrinsic stress - pressure curve for sputtering source characterization should be verified for a much broader spectrum of materials to establish a possible wider applicability.
References

Chapter 5

Texture formation in (Nb,Ti)N films

5.1 Introduction

Interest in the analysis of texture formation in (Nb,Ti)N films is motivated by a need to develop a reliable production line for THz SIS mixers. Because reactive ion-etching rates depend strongly upon the crystallographic plane exposed to the plasma, this manuscript focuses on determining the technological factors determining texture formation. The material of interest has a B1 rock-salt cubic crystal structure. Many researchers have observed similar dependence of texture on growth conditions for this class of materials [1-15]. However, only a few manuscripts are dedicated to a detailed texture characterization and an analysis of the technological factors determining the texture. This chapter is dedicated to a characterization of various factors contributing to texture formation in our films, and a comparison of the experimental results with existing models.

The question of whether a process reaches equilibrium or is instead limited by kinetics often arises in thin-film growth [10]. In general, there are two contradicting concepts, based on either a thermodynamic or a kinetic approach, which try to explain the formation of texture in the B1 type nitrides of transition metals [11].

Pelleg et al. propose a thermodynamic approach. They state that the degree of surface energy ($S_{hkI}$) is $S_{100} < S_{110} < S_{111}$, while the degree of strain energy per unit volume, ($u_{hkI}$), is $u_{111} < u_{110} < u_{100}$. Thus, if one assumes that the surface energy does not depend on film thickness and that the strain energy increases with it, one can then determine the total of the surface energy and strain energy for a given plane (hkl). Due to the driving force to minimize the total energy of the system, it would then be expected that (100) texture is preferred for relatively low film thickness, when the strain energy is less than the surface energy, with a change in texture with increasing film thickness to (110) and then to (111), because the strain energy starts to play a more dominant role in the determination of the total energy [12]. This theoretical prediction of strain-minimizing textures during film thickening was recently confirmed by the experimental observations of Oh et al. for 1.5 μm thick TiN films deposited by reactive rf-magnetron sputtering in a pure nitrogen atmosphere [13].

In contrast, Green et al. state that a texture formation can be determined by kinetic effects such as incident particle distributions, nitrogen overpressure, orientation-dependent surface adatom mobility, etc [14]. In particular they have shown that the presence of strain
and/or changes in the state of strain throughout the film thickness are not requirements for obtaining changes in preferred orientation. Petrov et al. associate changes in the texture of rf-bias-sputtered TiN films with ion channeling [15]. In this case, they explain a change from (111) to (100) texture with an increase in ion assistance by the fact that the planes corresponding to easy ion-channeling and lower sputtering yields have the highest probability to survive. Many researches use an approach based on a ratio of growth rates of different facets [16-19]. For a cubic lattice, an increase in the ratio of \{100\} and \{111\} facet growth rates results in a transition of texture from (100) to (110), and finally to (111). (It is interesting to note that, the texture evolution in this case is the same as in the thermodynamic model.) A transition from (111) to (110) texture occurs via an abundance of (11\gamma) textures, while a transition from (110) to (100) texture occurs via the abundance of (1\gamma0) textures, where 0<\gamma<1. However, factors like crystallographic defects, a lack of surface diffusion, or an instrumental function of the growth apparatus, etc., may hamper the growth of particular facets. In this case the crystal habit and film texture may differ from the one expected from the ratio of \{111\} and \{100\} facet growth [20]. A number of experimental reports are dedicated to specific in-plane orientations that are favored during thickening [11, 21-24]. This phenomenon may take place in magnetron deposition if the product of the sputtering pressure and substrate-target distance is small. In this case the trajectories of sputtered particles are almost ballistic, and the crystal facets facing the flux of the particles grow faster [11]. Finally, one of the most detailed studies of film texture and its correlation with the intensity and angle of incidence of the ion beam bombarding the surface of the growing film was performed by Alberts et al. [25]. Their study of biaxially textured films show that none of the models mentioned above can satisfactorily explain their experimental data.

5.2 Experimental

Films of (Nb,Ti)N are deposited by reactive magnetron sputtering in a Nordiko-2000 sputtering system with a base pressure of 4×10^{-5} Pa. This sputtering machine is equipped with a cryopump and a throttling valve, which together determine the process pressure, while the injection of Ar and N₂ gases is controlled by flow-meters. In order to avoid the hysteretic sputtering regime, the pumping rate is fixed at a high value of 750 l/s for all experiments [26]. Because the nitrogen injection is more than ten times lower than the argon injection in all experiments, the target material is primarily sputtered by argon atoms. A 99.8% pure alloy target with 30 at. % Ti and 70 at. % Nb is used. All films are sputtered by 300 W DC power and have a thickness of 480±20 nm. Wafers are fixed to the copper chuck (maintained at 20° C) with diffusion pump oil to stabilize the substrate temperature. The home-made 3 inch circular unbalanced sputtering source used for film deposition is described in details in the chapter dedicated to the comparison of the balanced and unbalanced sources. Gas densities are measured by inserting a small sampling pipe (attached to an external pressure gauge) between the sputtering source and the substrate. The details of this technique are discussed in the work of Rossnagel [27].

Films are deposited on 2 inch oxidized Si wafers. The center of the substrate chuck is located exactly below the center of the sputtering source. The position of the substrate on the chuck and the area of the substrate where the measurements are made, are carefully monitored to reveal the influence of technological factors that are responsible for in-plane texture formation. The center of the wafer is located 0.5 inch from the chuck center,
unless specifically mentioned in the text below. The central part of the wafer (approximately 1 inch in diameter) is used for all measurements. Note that this method of substrate loading allows to determine the contribution of self-shadowing effects to texture formation, as it is quite clear that self-shadowing effects will increase with increasing offset of the substrate from the center of the chuck, and will have azimuthal symmetry with respect to the center of the substrate chuck.

The stress in the films is evaluated by measuring the deflection of the wafer before and after film deposition with a profilometer. Assuming that the film thickness is much less than the substrate thickness, the film stress is then calculated using Stoney's equation [28], with the Young's modulus and Poisson's ratio taken from ref. 29. The transition temperature ($T_c$) is evaluated from the dependence of film resistivity on temperature. Film chemical composition is measured by Rutherford Back Scattering spectroscopy (RBS) using a 1 MeV He$^+$ beam for sample irradiation. Phase identification is based on XRD scans using a Rigaku D/max-Rc diffractometer. Texture measurements are performed with a Bruker-AXS D5005 diffractometer. Since most of our samples have a rotational symmetry of texture, a simple $\Psi$-scan procedure (a radial cross-section of the pole figure space) is also used for texture characterization. Cross-sectional TEM view samples are prepared by a standard technique - mechanical thinning down to 30 $\mu$m, followed by ion milling using a Gatan PIPS. The specimens are examined with a Philips CM200ST transmission electron microscope operated at 200kV. Atomic force microscope (AFM) Nanoscope III (MMAFM-1) produced by Digital instruments is used for film roughness characterisation.

5.3 Film properties vs. sputtering pressure

The nitrogen injection is optimized for a wide range of total sputtering pressures in order to obtain maximum $T_c$ of the (Nb,Ti)N films. The limits of the pressure range are determined by film degradation caused by destructive bombardment of the growing film by fast neutrals at low pressures, and high thermalization conditions at high pressures. Fig. 5.1 contains two sets of data for films deposited at the minimum substrate–target distance (4 cm) and the maximum substrate-target distance (8 cm). The deposition rates are $180 \pm 10$ nm/min and $80 \pm 5$ nm/min respectively. XRD analysis shows that all of the films have a B1 crystal structure. Both sets of data show similar behavior versus sputtering pressure. In general, the $T_c$ of the films is seen to have only a moderate dependence on the sputtering conditions, illustrating the well-known insensitivity of this value to structural defects in the B1 superconductors. Compressive stress also shows a typical behavior versus sputtering pressure for magnetron sputtering systems: it decreases significantly with increasing sputtering pressure. The variation in the intensity ratio of the [200] and [111] XRD lines indicates a substantial changes in the film structure. Finally, gas rarefaction becomes less pronounced at low pressures, since the hot particles of the sputtering yield have fewer collisions with the cold gas particles than at high pressures (Fig. 5.2). Furthermore, gas cooling during sputtering is more effective at the minimum substrate-target distance, due to an instrumental function of the sputtering system. Gas rarefaction is stronger at the maximum substrate-target distance. Film roughness is increasing with sputtering pressure. Note that, RBS indicates that all films have almost stoichiometric composition, with metal-nonmetal concentration ratio of 1±0.03, and a ratio of Nb and Ti in the deposited films that is the same as in the target.
Fig. 5.1 $T_c$, ratio of [200] and [111] XRD peaks, intrinsic stress, and roughness of (Nb,Ti)N films deposited at different substrate-target distance.
5.4 Film properties vs. nitrogen pressure

In this second experiment, the nitrogen injection is varied, while keeping the total sputtering pressure at fixed 6 mTorr. The substrate-target distance is set to the maximum distance (8 cm), and the limits of nitrogen injection are determined by a requirement that a B1-type crystal structure is produced. The resulting deposition conditions and film properties are illustrated in Fig. 2. As in the first experiment, T₀ is seen to have a moderate dependence on nitrogen injection (Fig. 5.3). Compressive stress has a very moderate increase with nitrogen injection (Fig. 5.3). This is presumably due to the fact that the fluxes of ions and fast neutrals bombarding the substrate surface are nearly independent of nitrogen injection, so that a reduction in deposition rate results in an increase in the effective intensity of the fluxes responsible for Ar peening. The deposition rate decreases with an increase in nitrogen injection, as is expected in reactive sputtering (Fig. 5.3). The ratio of the [200] and [111] XRD peak intensities strongly decreases with increasing nitrogen injection. This is a clear indication that substantial changes in film texture also take place in this experiment (Fig. 5.4). Film roughness is increasing with nitrogen injection. Despite the fact that the deposition rate decreases with an increase in nitrogen injection, gas rarefaction does not change. This is a clear indication that the particles of the sputtering yield become more energetic with an increase in nitrogen injection, causing the same gas rarefaction despite a reduction in numbers [30]. Rossnagel reports similar results [27]. He shows that the degree of gas rarefaction caused by the flux of hot sputtered particles depends mainly on applied power and that the target material has almost no influence on this phenomenon. Finally, it is found that increasing the nitrogen injection by a factor of two results in only a moderate increase in the nitrogen concentration in the films (Fig. 5.4), indicating that we are operating in the sputtering regime which the target surface is coated with nitride, and changes in nitrogen injection result primarily in a different depth of target nitridation [31,32].
Fig. 5.3. $T_c$, film stress, and deposition rate of the films deposited under different nitrogen injection.
Fig. 5.4. Surface roughness, ratio of [200] and [111] XRD peaks, and chemical composition of the films deposited under different nitrogen injection.
5.5 Film texture determination and analysis

Four samples, marked as p1-p4 in Fig. 5.1, are selected for texture examination in the experiment with sputtering pressure variation and maximum substrate-target separation. Because samples p1, p2, and p4 have a rotational symmetry of their texture, an illustration of only one $\Psi$-scan is sufficient, and they will be discussed first. Sample p1 has a well-pronounced (100) texture (Fig. 5.5). The peak in the [111] intensity curve at ca. 50° corresponds with the angle between the {111} and {100} planes in the fcc lattice. Sample p4 has a distinct (111) texture (Fig. 5.5). The peak in the [200] intensity curve at $\Psi=50^\circ$ is due to the same reason. Likewise, the peak in the [111] intensity curve at ca. 70° is due to the fact that the angle between {111} equivalent planes is 70.4°. Sample p2 consists of a mixture of (100) and (311) textured grains (Fig. 5.5). The intense peak at

![Fig. 5.5 $\Psi$-scans for the samples p1, p2, and p4.](image-url)
Ψ=30°, with a stretched shoulder towards Ψ=80° on the [111] intensity curve is due to the merging of peaks of (311) textured grains at Ψ=29.5° and 58.5°, plus a peak of (100) textured grains at Ψ=54.7°. Similar reasons cause peaks on the [200] intensity curve at Ψ=20° and 70°.

Sample p3 does not have a rotational symmetry of texture. For this reason, a pole figures of the [111] reflection of samples p3 and p3a, and their location on a substrate chuck, are illustrated in Fig. 5.6 and Fig. 5.7. It is seen that sample p3 has an in-plane texture that is oriented in the direction of vector R, which starts in the center of the chuck and goes through the center of the measurement zones. In order to verify the hypothesis that self-shadowing is the case of this in-plane texturing, the sample p3a is deposited under the same conditions as sample p3, but with a larger off-center loading position (Fig. 5.7). This sample is found to show a more pronounced in-plane texture, because the sputtering yield flux is more oblique. Samples p3 and p3a have (211)[111] texture, since they have maximum intensities at Ψ=20° and φ=0°, Ψ=60° and φ=110°, Ψ=60° and

Fig. 5.6 Pole figures of [111] reflections of the samples p3 and p3a.
Fig. 5.7 Location the samples p3 and p3a on the chuck.

φ=250°. Finally, in order to illustrate the dependence of texture evolution on sputtering pressure, Fig. 5.8 shows a Ψ-scan of sample p3. This Ψ-scan is made in the direction perpendicular to the radius vector R, in order to minimize the contribution of the self-shadowing effect. The peaks at Ψ=30° and 60° on the [200] intensity curve correspond with the angles between the [100] and [211] planes. Reflections of (211) textured grains also cause peaks on the [111] intensity curve at Ψ=20° and 60°.

The fact that in-plane texture is observed only for sample p3 in the experiment with pressure variation and a maximum substrate-target distance, because this phenomenon is a balance of two factors in this case. On one hand, the film roughness (Fig. 5.2) decreases with decreasing sputtering pressure, suppressing self-shadowing. The (100) textured grains have an almost flat surface in comparison with the (111) textured grains [17,33]. On the other hand, reducing the sputtering pressure makes the flux of the sputtered particles less diffuse, facilitating self-shadowing. As a result the in-plane texture is only observed for the sample p3.

Fig. 5.8 Ψ-scan for the sample p3.
A similar texture dependence on sputtering pressure is observed at the minimum substrate-target distance. Likewise, examining the film texture versus nitrogen injection shows similar texture evolution. A detailed examination of the texture reveals that the film deposited with the lowest nitrogen injection has a texture similar to the texture of sample p2, while the film deposited with the highest nitrogen injection has a texture similar to that of sample p3. In other words, increasing the nitrogen injection affects the film texture in the same way as an increase in sputtering pressure.

A cross-sectional TEM image of the film sputtered under a total pressure of 6mTorr and 3 sccm nitrogen injection (sample p3 in Fig. 5.1 and Fig.5.2) is shown in Fig. 5.9. The cross-section is made in the same plane as the Ψ-scan (Fig.5.8). The cross-sectional TEM bright image is taken in a slightly under-focused regime to emphasize the grain boundaries (Fig. 5.9a). Selective area diffraction is shown in the insert of Fig.5.9a. It reveals also the presence of a weak texture indicated by intensity variations in the

![TEM Image](image_url)

**Fig. 5.9** Cross-sectional TEM images in the bright (Fig. 5.9a) and dark (Fig. 5.9b) fields of p3 sample. SAD diffraction image is shown in the insert of the Fig. 5.9a.
diffraction rings. The [111] reflection from the grain marked with an arrowhead in Fig. 5.9a is used to make a dark field image (Fig. 5.9b) to illustrate the morphological texture. As seen in Fig. 5.9, the in-plane grain size increases with film thickness as a result of competitive growth [14,34]. The image illustrated in Fig. 5.9 is typical for all of the studied films. It is interesting to note that, in contrast with the case of texture determined by competitive growth, that is mentioned in the introduction, the change from [111] to (100) texture goes via the abundance of (1\gamma\gamma) textures, where 0\leq\gamma\leq1. In other words, the system makes a "short cut," bypassing (110) texture.

As seen from Fig. 5.1 and Fig. 5.3, an increase in compressive stress correlates with a change from [111] to (100) texture. Thus, the thermodynamic model does not describe our case, since it predicts the opposite behavior. As has been discussed in the chapter dedicated to the sputtering source optimization, ion assistance is quite weak and has a very moderate impact on film properties. This allows us to exclude the ion-channeling approach as well. As seen from Fig. 5.1, the properties of films sputtered at minimum substrate-target distance are almost equivalent to the properties of films sputtered at maximum substrate-target distance and twice lower gas concentration. This is a clear indication that thermalization of the sputtering yield is a determining factor, i.e. the energy of the adatom is the factor that determines the process of texture formation [35]. Increasing the adatom energy causes the change of texture from [111] to (100) in the experiment with pressure variation. This means also that surface diffusion is not suppressed by increasing the adatom arrival rate [36]. However, as was mentioned previously, the adatom energy increases as the nitrogen injection increases, but the system is driven towards [111] texture. In other words, the film chemical composition has a very strong impact on texture development, overriding the effect of adatom energy.

### 5.6 Conclusions

The texture of (Nb,Ti)N films is examined over a wide range of technological parameters. Film chemical composition, adatom energy, and crystal habit are identified as determining factors for texture formation. The contribution of in-plane texturing due to self-shadowing is separated by off-center substrate loading. Varying the sputtering pressure for different substrate-target distances reveals that, increasing adatom energy results in a change of texture from [111] to (100) for a constant chemical composition. The thermodynamic model, based on a balance of stress energy and surface energy, is not applicable in this case, since minimizing the overall energy predicts a transition from (100) texture to [111] texture as compressive stress increases, while our films show an opposite behavior. In addition, this experiment indicates that deposition rate does not affect the film growth. However the process of texture formation is not exclusively kinetically limited. Despite the fact that an increase in nitrogen injection results in an increase in the adatom energy, the system is driven towards [111] texturing. TEM analysis shows that film texture is formed through a process of competitive growth. Furthermore, despite the fact that adatom energy and film chemical composition are factors with different origins, their impacts on film texture evolution are the same. Finally, the transition from [111] to (100) texture occurs via an abundance of (1\gamma\gamma) textures, where 0\leq\gamma\leq1, while the classical model, based on competitive growth of \{111\} and \{100\} facets, predicts a transition from [111] to (110) texture via an abundance of (11\gamma) textures and the transition from (110) to (100) via the abundance of (1\gamma0) textures. The origin of this difference is yet to be determined.
References


Chapter 6

NbN/AlN/NbN SIS junctions

6.1 Werthamer model of tunneling in SIS junctions

Tunnel Hamiltonian approach has been successfully used for a description of a current flowing through the tunnel junction [1]. Further development of this method resulted in a creation of the microscopic theory of tunneling effect for the general non-static case. This theory enables to calculate junction current for an arbitrary applied voltage $V(t)$ [2, 3]. SIS junction current can be written as follows:

$$I(t) = \text{Im} \int_\infty^\infty d\omega \int d\omega' \left\{ W(\omega)W(\omega') \exp \left[ i(\omega + \omega' + \omega_j/2) t \right] J_p(\hbar(\omega + \omega_j/2)/e) + \right\}$$

$$W(\omega)W^*(\omega') \exp \left[ i(\omega - \omega') t \right] J_q(\hbar(\omega' + \omega_j/2)/e)$$

where the function $W(\omega)$ is determined by the phase difference between the junction electrodes versus time

$$\exp(i\phi(t)/2) = \exp \left[ \frac{i e}{\hbar} \int V(t) dt \right] = \int W(\omega) \exp(i(\omega_j + \omega)t) d\omega$$

and $\omega_j = 2e\bar{V}/\hbar$, $\bar{V}$ -average component of the applied voltage. Functions $J_{p,q}$ are determined by the properties of the superconducting electrodes. If the order parameter is the same in every point of electrode, than these functions can be derived as follows:

$$\text{Re} J_p(V) = \frac{1}{2eR_N} \int d\epsilon \frac{e}{2kT} \left[ \text{Im} F_1^R(\epsilon) \text{Re} F_2^R(\epsilon + eV) + \text{Re} F_1^R(\epsilon + eV) \text{Im} F_2^R(\epsilon) \right]$$

$$\text{Im} J_p(V) = \frac{1}{2eR_N} \int d\epsilon \left[ \text{th} \left( \frac{\epsilon - eV}{2kT} \right) - \text{th} \left( \frac{\epsilon}{2kT} \right) \right] \text{Im} F_1^R(\epsilon + eV) \text{Im} F_2^R(\epsilon)$$
\[
\text{Re } J_q(V) = \frac{1}{2eR_N} \int d\epsilon \left[ \frac{\epsilon}{2kT} \log \left( \frac{1 + \exp \left( -\frac{\epsilon - eV}{2kT} \right) + \exp \left( -\frac{\epsilon + eV}{2kT} \right)}{1 + \exp \left( -\frac{\epsilon}{2kT} \right) + \exp \left( -\frac{\epsilon + eV}{2kT} \right)} \right) \right] \text{Re } G_1^R(\epsilon) \text{Re } G_2^R(\epsilon + eV) + \text{Re } G_1^R(\epsilon + eV) \text{Im } G_2^R(\epsilon) \\
\text{Im } J_q(V) = \frac{1}{2eR_N} \int d\epsilon \left[ \text{th} \left( \frac{\epsilon - eV}{2kT} \right) - \text{th} \left( \frac{\epsilon}{2kT} \right) \right] \text{Im } G_1^R(\epsilon + eV) \text{Im } G_2^R(\epsilon)
\]

Where subscripts “1” and “2” correspond to the left and right electrodes, \( R_N \) is the specific resistance of the junction in a normal state, \( F_{1,2}^R(\epsilon), G_{1,2}^R(\epsilon) \) integrated over energy Green functions. In the case of homogenous electrodes these functions can be written as:

\[
G^R(\epsilon) = \frac{\epsilon}{\sqrt{\Delta^2(T) - (\epsilon + i0)^2}} \\
F^R(\epsilon) = \frac{\Delta(T)}{\sqrt{\Delta^2(T) - (\epsilon + i0)^2}}
\]

If the Mc'Camber parameter \( \beta = \frac{2e}{\hbar} I_C R_N^2 C \), where \( I_C \) and \( C \) are a critical current and capacitance of the junction \( \beta \geq 10 \) then the voltage at the junction is almost static and the expression for the junction current can be considerably simplified: \( I(t) = \text{Re } J_p(V) \sin(\phi) + i \text{Im } J_p(V) \cos(\phi) + i \text{Im } J_q(V), \varphi = 2eVt/\hbar + \phi_0 \), where \( \text{Re } J_p(V) \) – amplitude of the Josephson super current, \( \text{Im } J_q(V) \) amplitude of the dissipative component of this current determined by the interference of the Cooper pairs and quasiparticles, \( \text{Im } J_q(V) \) – quasi-particle current. Fig. 6.1. illustrates a Voltage-Current characteristic (VCC) of a quasi-particle current flowing through SIS junction versus different temperatures [4]. Increase in temperature results in decrease of the gap voltage and sub-gap current.

**Fig. 6.1.** Quasi-particle current voltage-current characteristics of SIS junction according Werthamer model versus different temperature, where \( t = T/T_C \). Modified from ref. 4.
6.2 Proximity effects in SIS junctions

The results of classical tunneling theory mentioned above describe the properties of the SIS junctions made on the basics of "soft" superconductors like Sn, Pb, In or their alloys like PblnAu or PbIn. However this model can not describe the most interesting case from the practical point of view. VCC's of SIS junctions based on "hard" superconductors like Nb and NbN have additional features compare to the classical model. For instance they show so-called "knee" structure, diffuse rise of the quasi-particle current at the gap voltage \((\Delta_1+\Delta_2)/e\), considerable quasi-particle currents at the voltages below the gap voltage. One of the main reasons of these features is the presence of a normal metal layer between a superconducting electrode and a tunnel barrier. Most of SIS junctions have SINS or SNINS structure. For example this kind of layers occurs in SIS junctions based on Nb/Al-AlO_x/Nb try-layer, since the oxidized aluminum layer is much thinner compare to the layer that is needed to wet completely Nb base electrode.

As certain attempt has been made to describe SINS structures theoretically with the help of modified tunnel Hamiltonian. The densities of states are modified at the tunnel barrier compare to the BCS ones. Mc'Millan's model is one of the widely used for the description of the superconductivity at the SN interface [5,6]. However the main assumptions of this model like low transparency of the SN interface and low thickness of the S and N layers compare to the coherence length make it unpractical, since these conditions do not occur in most of the SN structures.

M. Yu. Kupryanov and A. M. Golubov have developed a theoretical model of SINS junctions that can be applied to a broad spectrum of junctions. More over this model describes conditions that are realized in frequently used SINS junctions. This approach is based on the quasi-classical Uzadel equations [7]. The boundary conditions developed in ref. 8 resulted in a development of an adequate model for the superconductivity at the SN interface. The influence of the normal layers in the SINS structures for the case of "dirty" limit can be described by three parameters: \(\frac{T'_C}{T_C}\) - ratio of transition temperatures of N and S layers, \(\gamma_M = \frac{\rho_S \xi_S}{\rho_S^* \xi_S^*} \cdot \frac{d}{\xi_s^*}\) - characterizes the degree of superconductivity suppression in SN structure, and \(\gamma_{BM} = \frac{R_B}{\rho_S^* \xi_S^*} \cdot \frac{d}{\xi_s^*}\) characterizes the degree of SN interface transparency. Where \(\rho_S\) and \(\xi_S\) (\(p\) and \(\xi\)) - specific resistance and coherence length of the superconductor layer (normal layer), d - thickness of a normal layer, \(R_B\) - specific resistance of SN interface. For example typical values for Nb/Al interface in the Nb/Al-AlO_x/Nb try-layer are: \(\gamma_M = 0.1\) and \(\gamma_{BM} = 0.1\) [9].

In order to illustrate the influence of the proximity effect on a shape of a quasiparticle VCC of the SINS junction a computer simulations are performed with the help of a software code developed by S. V. Polonskii [8]. Fig. 6.2 and Fig. 6.3 illustrate the influence of the proximity effect on VCC's and densities of states at the boundaries.
Fig. 6.2. Voltage – current characteristics of SINS junctions and densities of states at the boundaries of SN electrodes for $T=0.5 T_c$, $T_c / T_c = 0.25$, $\gamma_{BM} = 0$, and $\gamma_M = 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.015, 0$ (curves 1-8 correspondingly).
Fig. 6.3. Voltage – current characteristics of SINS junctions and densities of states at the boundaries of SN electrodes for $T=0.5 \ T_c$, $\gamma_\omega = 0.1$, $\gamma_\Omega=0$, and $T_c^*/T_c = 0, 0.05, 0.1, 0.3, 0.5, 1$ (curves 1-6 correspondingly).
of SN electrodes. In particular, Fig. 6.2 illustrates the influence of the normal layer thickness. As $\gamma_n$ increases the density of states and the current rise at gap voltage rise become more diffuse, sub-gap leakage current increases, the “knee” structure reaches its maximum at $\gamma_n$ about 0.1. Similar changes take place as the $T_c$ of the normal layer decreases (Fig. 6.3).

6.3 Effects of multiple Andreev reflections in SIS junctions

The technological procedure of tunnel barrier formation is not perfect in most of the cases. This results in the formation of the channels with high transmission coefficients [10,11]. This enables the process of Multiple Andreev reflections (MAR). Quasi-particles are transferred at voltages lower than $2\Delta/e$ (Fig. 6.1) by a multiple reflection process involving breaking and creation of Cooper pairs. Since this process involves multiple passes, then current developed by this process will be proportional to $(\sqrt{T})^n$, where $n$ is a number of Andreev reflections, $\sqrt{T}$ is the barrier transmittance (or in our case pinhole transmittance). Therefore MAR requires the presence of parts in a tunnel barrier with high transmittances. Fig. 6.4 illustrates VCC’s of S-S contact with different values of transmittances at zero temperature [12]. Increase in tunnel barrier transmittance results in activation of higher order MAR based tunneling processes. The current increases at voltages $2\Delta/ne$, produced by MAR, get more pronounced as transmittance increases. At high transmittances VCC’s approach SNS limit.

![Graph showing the relationship between $I_o/(2eA\lambda)$ and $V/\Delta$ with different transmittances labeled.](image)

**Fig. 6.4.** VCC’s of S-S contacts with different values of transmittances at zero temperature. Modified from ref. 12.
6.4 Fabrication procedure and analysis

At the first stage an amorphous Al$_2$O$_3$ buffer layer is sputtered on the whole Si (100) wafer. This buffer prevents the etching of the wafer during further fabrication. Al$_2$O$_3$ films are sputtered from the Al$_2$O$_3$ ceramic target by RF-discharge in a high vacuum system Leybold AG L-560 UV with the base pressure of 5×10$^{-5}$ Pa. Ion gun etching is used in this system prior every technological process to improve adhesion of the layers. The deposition conditions of all layers are summarized in the Table. 6.1. The sequence of technological steps is illustrated on the Fig. 6.5. The same sputtering system is used

Table 6.1. Growth conditions of the layers. Different thickness of the NbN layers is marked by BE, TE, C. Acronyms BE, TE, C correspond to the base electrode of SIS junction, the top electrode of SIS junction, and the counter electrode.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Al$_2$O$_3$</th>
<th>NbN</th>
<th>AlN</th>
<th>SiO</th>
<th>Nb</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition system</td>
<td>L-560 UV</td>
<td>L-560 UV</td>
<td>L-560 UV</td>
<td>Z-400</td>
<td>A-700</td>
<td>A-700</td>
</tr>
<tr>
<td>Deposition technique</td>
<td>RF magn.</td>
<td>DC magn.</td>
<td>DC magn.</td>
<td>therm. evap.</td>
<td>DC magn</td>
<td>RF magn.</td>
</tr>
<tr>
<td>Power, W</td>
<td>500</td>
<td>600</td>
<td>60</td>
<td>-</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>Ar injection, sccm</td>
<td>100</td>
<td>130</td>
<td>100</td>
<td>-</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>$N_2$ injection, sccm</td>
<td>-</td>
<td>14</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total pressure, mTorr</td>
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<td>12</td>
<td>14</td>
<td>-</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Thickness, nm</td>
<td>100</td>
<td>200 BE</td>
<td>100 TE</td>
<td>500 C</td>
<td>2</td>
<td>250</td>
</tr>
<tr>
<td>Deposition rate, nm</td>
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<td>90</td>
<td>2</td>
<td>2</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>Substrate-source dist., cm</td>
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<td>7</td>
<td>7</td>
<td>15</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
for NbN/AlN/NbN try-layer deposition. It is deposited by DC magnetron reactive sputtering in one run via the photoresist mask defining the geometry of the base electrode. The argon injection is optimized to produce stress free NbN films, while nitrogen injection to achieve maximum $T_c$ and $\delta$-NbN phase. Intrinsic stress is estimated from the bend of glass wafers having thickness 0.2 mm after NbN sputtering [13]. Film $T_c$ is evaluated from the dependence of film resistivity versus temperature. Details of the optimization procedure are widely discussed in the third chapter. AlN layer

**Fig. 6.5. Technological steps of the SIS junction fabrication process.**
sputtering conditions are optimized to produce low deposition rate, stable glow discharge, and hcp crystal structure. Phase identification of AlN and NbN is carried out with θ-2θ XRD scans performed on Rigaku RU-300 Bragg-Brentano diffractometer.

The junctions are patterned by reactive ion etching in a CF₄ + O₂ mixture via photoresist mask. The etching automatically stops on AlN layer. In order to prevent shorts on the junction edges the next masking layer for isolation has smaller area than junction size on top of the NbN column formed by etching. The isolating layer (SiO) is evaporated out of a tungsten boat. This layer is produced in the Leybold Z-400 vacuum system with the base pressure of 2×10⁻⁴ Pa. Light RF sputter-etching is used prior SiO evaporation to achieve good adhesion of the insulating layer. The top wiring NbN layer is determined by lift-off procedure as well. This layer is sputtered in the same sputtering system as the junction try-layer. The last step is the Au contact pads lift-off definition. Nb adhesion sub-layer is used to achieve good adhesion of Au. The Nb-Au double-layer is sputtered in the Leybold A-700 sputtering system with the base pressure of 2×10⁻⁴ Pa. Nb films are sputtered with DC-magnetron, while Au layer with RF-magnetron. Light RF sputter etching is used prior film deposition to achieve good adhesion as well.

Fig. 6.6 demonstrates the typical current-voltage characteristic (CVC) of the tunnel junction with 67 μm² area. The CVC is measured by the bias power supply operated in the “current source” regime. High sub-gap current can be associated with both of SIS “diseases”, i.e. pinholes in the tunnel barrier and proximity effect. Proximity effect is cased by poor quality of the bottom layers of a top electrode. T_c of 4 nm thick NbN layer deposited on Si wafer buffered with AlN does not show superconductivity at liquid helium temperature. This is a sufficient indicative of a presence of the proximity effect, since a coherence length in this material is 4-5 nm. A number of researchers report similar results [14, 15]. For instance, Murdruk et al. [14] observe rapid degradation of T_c in [NbN/AlN]₅ multi-layers with reduction of NbN thickness. Atomic

![Current-Voltage characteristic of NbN/AlN/NbN tunnel junction at 4.2 K.](image-url)
force microscopy (AFM) image of the bottom junction electrode, obtained with the help of “Autoprobe CP” AFM machine (“Park Scientific Instruments”), is illustrated on Fig. 6.7. The surface has sharp peaks up to 5 nm, which inevitably lead to pinhole creation, since the thickness of AlN layer is only 2 nm. Pinhole issue in NbN based junctions is widely discussed in a thesis of P. Dieleman [16]. A. Shoji suggested the best solution of this problem up to now [17]. NbN films grow on 100 MgO wafers in van der Merve mode [18]. The surface of NbN films is almost flat in this case. Moreover utilization of thin AlN tunnel barriers (=1 nm) enables to produce multi-epitaxial try-layers [19].

Fig. 6.7. AFM image of SIS bottom electrode.

6.5 Conclusions

The set of the optimal technological parameters for the fabrication NbN/AlN/NbN tunnel junctions has been found. The electrodes consist of the δ' - NbN phase with $T_c=14.7\,K$. The junction try-layer is successfully obtained by DC magnetron sputtering without intentional substrate heating. The proximity effect and pinholes in the tunnel barrier result in a marginal junction quality. Low $T_c$ of bottom layers of the top junction electrode results in the proximity effect. Sharp peaks on a surface of the bottom
electrode cause pinholes in the tunnel barrier, since they have a height 2-3 times exceeding the thickness of AlN tunnel barrier.

References

Chapter 7

Nb/Al-AlN/Nb tunnel junctions

7.1 Introduction

Pushing the operation of SIS heterodyne mixers towards THz frequencies requires strip lines with low losses at these frequencies and high quality SIS junctions with lower $R_nA$ values and higher gap voltage compared to the SIS junctions based on Nb/Al-AlO$_x$/Nb try-layer [1-10]. More over, the utilization of SIS junctions with low $R_nA$ values allows us to design SIS mixers with lower noise temperatures and broader bandwidths. It has been shown that SIS junctions with the AlN$_x$ tunnel barriers are superior over the AlO$_x$ based tunnel junctions in these respects [5]. This method employs RF glow discharge in a nitrogen atmosphere for AlN$_x$ tunnel barrier production [10].

The study of metal surface nitridation in a glow discharge was begun almost a century ago. Many different technological parameters have been identified as key parameters: metal temperature, glow-discharge type, the energy spectrum of bombarding ions and fast neutrals, gas composition, etc [11]. A successful method of the AlN$_x$ tunnel barrier growth, based on this principle, has been implemented by T. Shiota et. al. in Nb/Al-AlN$_x$/Nb SIS junctions [12]. Furthermore this process has been studied in greater detail and compared with the Nb/Al-AlO$_x$/Nb process by R. Dolata et. al [13]. However, this process fails to produce the high quality SIS junctions with low $R_nA$ value [14]. This is due to the fact that the substrate located on a driven electrode is exposed to a very energetic and intense flux of ions during Al layer nitridization. Nitrogen ions not only perform nitridation Al layer, but also damage the growing AlN$_x$ layer [15]. The breakthrough has been achieved by B. Bumble et. al [10]. They proposed to attach a substrate to a grounded electrode located parallel to a driven electrode. This allows a substantial reduction of the density and energy of bombarding ions. A properly designed system with a capacitively coupled driven electrode allows us to achieve the plasma potential almost equal to the floating potential [16]. In this case the bombarding ions activate the surface reaction without damaging the surface [15]. This chapter is dedicated to an experimental verification and detailed characterization of this method since it has been implemented only in one laboratory.
7.2 Experimental

The junctions are produced in a Nordiko-2000 sputtering system with a base pressure of $4 \times 10^{-5}$ Pa. This sputtering machine is equipped with a cryopump and a throttling valve, which together determine the process pressure, while the injection of Ar and N$_2$ gases is controlled by flow meters. All films are deposited by 3 inch Nordiko DC magnetrons at maximum substrate – target distance for this system (8 cm) to achieve maximum uniformity of the layers. Wafers are fixed to the copper chucks, maintained at 20° C with diffusion pump oil to stabilize the substrate temperature.

Following the concept of minimization of the energy and intensity of the ion flux bombarding the Al surface during a process of nitridation, the following system is designed. The driven electrode consists of the 4 inch Nordiko magnetron sputtering source with removed magnets. In other words, the removal of magnets converted the sputtering source into an RF diode sputtering system. Taking into account that a sputtering of a target material will take place in any case, an Al target 99.99 % pure was installed in this source. The target size is a trade off between to two contradicting factors: the target area has to be maximized to produce maximum uniformity of the ion flux towards the substrate surface, but on the other hand minimization on the target area results in reduction of the plasma potential [15]. The latter consideration is fulfilled almost automatically since plasma non-confined by the magnetic trap is in contact with an area in the sputtering chamber which is much bigger than the cathode area. The electrode is connected to the RF generator via the Nordiko matching unit providing the capacitive coupling of plasma.

The substrate chuck is not grounded in our system and remains permanently connected to a matching unit and RF generator. This circumstance results in an additional issue of concern. An equivalent electric circuit is illustrated in Fig. 7.1. Various types of resonance may occur in this system. For example, a very high negative substrate bias of a substrate chuck may occur in this type of systems, due to the series resonance between an inductive tuning network and a capacitive substrate sheath [17, 18]. These factors are investigated carefully by manually changing the substrate matching unit impedance and measuring the substrate potential. The impedance of the substrate matching unit has been selected to avoid all these possible resonances.

The Langmuir probe, manufactured by Scientific Instruments, is employed for plasma characterization. The probe is located 2 cm above the center of the substrate chuck. The flux of nitrogen ions bombarding the substrate during the nitridation procedure is characterized by two key parameters: the voltage drop across the substrate sheath ($V_{sh}$), measured as a difference between the substrate and plasma potentials, and the ion current density injected into the sheath ($I_i$). Characterization of the plasma properties by the Langmuire probe revealed that $V_{sh}$ values are very close to the plasma floating potential, indicating that the developed system produces the least possible plasma potential.

The tunnel junctions are produced by the selective niobium anodization process (SNAP) [19]. This recipe provides the fastest and the easiest way of junction production. A cross-section of SIS junction produced by the SNAP process is illustrated in Fig. 7.2. The production process consists of 3 steps: (1) A Nb/Al-AIN$_x$/Nb try-layer is deposited in one run on a Si wafer. (2) A photoresist mask is formed to define 10 $\mu$m$^2$ junctions. A subsequent anodization up to 80 V of the top Nb layer and Al-AIN$_x$ layers completes the junction formation. (3) Top wiring, consisting of Nb and Au layers, is sputtered via a
Fig 7.1. Electrical model for experimental system.

Lift-off photoresist mask. The layer thicknesses and sputtering conditions are listed in Table 7.1. The voltage-current characteristics (VCC) of the junctions are measured in a liquid helium and characterized by a software program developed by Ermakov et. al [20]. The VCC are characterized on the basis of two key parameters: the specific junction resistance, $R_sA$ value, and quality factor, $R_{sg}/R_n$ (the ratio of sub-gap and normal resistances). $R_nA$ value is used rather than critical current density for junction characterization because this parameter is much easier and faster to measure. This circumstance is of great importance for us, since our research is based on the processing of a large amount of junctions. More over, the critical current density can be calculated from the gap voltage by the Ambegaokar-Baratoff relation [21].
Table 7.1. Sputtering conditions of the layers used for SIS junction production.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Power (W)</th>
<th>Ar pressure (mTorr)</th>
<th>Deposition rate (nm/min)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb bottom electrode of SIS junction</td>
<td>300</td>
<td>8</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>Al layer</td>
<td>40</td>
<td>8</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>Nb top electrode of SIS junction</td>
<td>300</td>
<td>8</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Nb top wiring</td>
<td>300</td>
<td>8</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>Au layer</td>
<td>100</td>
<td>8</td>
<td>180</td>
<td>50</td>
</tr>
</tbody>
</table>

Fig 7.2. Cross-sectional view of SIS junction produced by selective niobium anodization process.

7.3 Results and discussion

The influence of nitrogen pressure, discharge power, and nitridation time on junction properties is investigated in this chapter. The investigation of the dependence of junction properties versus nitridation time has been carried out under a nitrogen pressure fixed at 50 mTorr and an applied power fixed at 30 W. These settings result in the following nitrogen ion flux parameters: $J_i = 0.22$ A/m$^2$ and $V_{an} = 21$ V. Fig. 7.3 illustrates the dependence of $R_nA$ and $R_{sg}/R_n$ versus nitridation time. Both curves show monotonic increase with time and a certain plateau at the beginning. Such a behavior is due to the combination of two processes: nitridation of Al layer and deposition of the AlN$_x$ material. The deposition of AlN$_x$ equals to 6 Å/h and is a monotonous process in time. However, nitridation of the Al layer reaches saturation, as it has been shown by Bumble et al [10]. Park et al have observed similar behavior for the Si nitridation process [22].

Variation of the nitrogen pressure, keeping the other parameters fixed (30 W applied power, 7 minutes nitridation time) does not result in a significant changes in the $R_nA$ values. The tunnel barrier formation is almost exclusively determined by nitridation in this experiment, since the duration of the process is too short to result in a significant thickness of the deposited AlN$_x$ material. All junctions, having tunnel barriers produced in the interval of 10-50 mTorr, have $R_nA = 4.4 \pm 1.5$ $\Omega \cdot \mu$m$^2$ and $R_{sg}/R_n = 8.4 \pm 1.5$. The absence of any substantial changes in junction properties in this experiment is due to a moderate dependence of nitrogen ion flux on pressure (Fig. 7.4). The ion density slightly increases with pressure, while the sheath voltage slightly decreases with pressure.
Fig. 7.3. Junction properties versus nitridation time. Nitrogen pressure during Al layer nitridation is kept at 50 mTorr for all data points. Applied power during Al layer nitridation is kept at 30 W for all data points.

An increase of the applied power, keeping the other parameters fixed (50 mTorr nitrogen pressure, 7 minutes nitridation time) results in an increase in $R_n A$ and $R_{np}/R_n$ values (Fig. 7.5). The deposited thickness of the AlN$_x$ material is also negligible in this experiment, due to the short duration of the process. Nitrogen ion flux characteristics are illustrated in the Fig. 7.6. The ion density considerably increases with increase in applied power, while the sheath voltage shows a very moderate decrease.

Typical junction VCC are illustrated on Fig. 7.7 The critical current is suppressed by a magnetic field. As the current density increases the sub-gap leakage also increases, indicating that thinner tunnel barriers contain more defects. The gap voltage is gradually reduced with an increase in $R_n A$ values due to self-heating of the junctions. The same phenomenon causes the back bending of the VCC at the gap voltage for the junctions with low $R_n A$ values. The bends of the VCC curve at 2.0 mV and 3.5 mV in Figs. 7.7a and 7.7b correspondingly is due to the transition of the junction wiring to the normal state. Fig.7.8 illustrates the dependence of $R_{np}/R_n$ versus $R_n A$ in the interval of 0-40 $\Omega \cdot \mu m^2$ for all junctions produced in these experiments. It is interesting to note that despite the different conditions of the tunnel barrier formation there is a well-defined correlation between the junction quality and $R_n A$ value.

The nitrogen ion flux, bombarding Al surface, consists mainly of N$_2^+$ ions and a small fraction of N$^+$ ions of the order of a few percents [23]. N$_2^+$ ions undergo dissociation on the substrate surface with equal splitting of the retaining energy between nitrogen atoms due to so called “shrapnel effect” [24]. If it is taken into account, that the initial energy of N$_2^+$ ions in our system does not exceed 21 eV and the dissociation energy of nitrogen is 9.7 eV, than the energy of nitrogen atoms on the surface in this process will be about a
Fig. 7.4. Voltage drop across the substrate sheath and ion current density injected into the sheath. Applied power is kept at 30 W for all data points.

Fig. 7.5. Junction properties versus applied power. Nitrogen pressure is kept at 50 mTorr for all data points.
few eV, which is clearly insufficient for implantation into the Al layer [25]. In contrast, N\textsuperscript{+} ions with the energy of 20 eV, according to “SRIM” program simulation, have almost zero reflection coefficient and a projected range of 5 Å into Al layer and 6 Å into AlN layer [26]. The channeling effects are not taken into account, because the texture of a thin Al layer on a rough Nb surface is very broad and therefore this effect may affect a very small fraction of Al grains [27, 28]. If it is assumed that the ion flux contains 1 % of N\textsuperscript{+} ions, than the density of implanted nitrogen atoms will equalize with the density of Al atoms on the (111) plane in 7 minutes in the experiment with nitridation time variation (Fig. 7.3). Since this time interval is of the same order of magnitude as the duration of the tunnel barrier formation, and the tunnel barrier itself consists of a few monolayers of AlN\textsubscript{x}, it is concluded that the flux of atomic nitrogen ions is a major initial factor in tunnel barrier formation. On the other hand, the projected range of implanted nitrogen atoms is about two times lower compare to the typical tunnel barrier thickness [29]. This is a clear indication that nitrogen diffusion in Al and/or in AlN\textsubscript{x} facilitated by plasma heating is a finalizing process in tunnel barrier formation. The presence of a diffusive component in this process is well recognized in a number of theoretical and experimental works [30-32]. Thus a saturation of nitried depth of Al layer in time (Fig. 7.3) is due to the fact that nitrogen, incorporated into the stoichiometric AlN layer, diffuses out under a strong temperature gradient on the substrate surface developed by plasma heating [22, 30-32]. Additional confirmation of the diffusive nature of AlN\textsubscript{x} tunnel barrier formation can be drawn from the experiment with applied power variation. An increase in the tunnel barrier thickness in this experiment is due to an increase in power dissipated on a substrate surface, since the $V_{\text{sh}}$ is almost constant and $I_{I}$ increases almost proportionally to the applied power (Fig. 7.6). It is interesting to make a remark about the energy budget of

Fig. 7.6. Voltage drop across the substrate sheath and ion current density injected into the sheath. Nitrogen pressure is kept at 50 mTorr for all data points.
Fig. 7.7. Typical VCC of SIS junctions with different $R_nA$ values. The size of all junctions is $10 \, \mu m^2$.

Fig. 7.8. Junction quality parameter $R_{sg}/R_n$ versus specific junction resistance $R_nA$.

this system. The power density dissipated on the substrate, estimated as a product of $J_l$ and $V_{sh}$, is less than 1% of the minimum power, that has to be applied to the driven electrode for a sustaining of plasma (7 W). Therefore, there is a fundamental difference between the process of Al nitridation on the driven electrode and on the electrode parallel to the driven electrode.
7.4 Conclusions

The system for the production of high quality Nb/Al-AlN/Nb tunnel junctions with low $R_n A$ values is developed and characterized. RF-glow discharge in the atmosphere of nitrogen is employed for Al layer nitridation. Locating the substrate on the electrode parallel to the driven electrode allows to achieve a very mild bombardment of the substrate surface by nitrogen ions accelerated by the plasma potential. The influence of various technological factors on junction properties has been examined. An increase in nitridation time results in an increase of junction resistance. An increase in AlN$_x$ tunnel barrier thickness in this experiment is due to the processes of Al layer nitridation and deposition of the AlN$_x$ material. Variation of nitrogen pressure, keeping the other parameters fixed, does not affect the junction properties, while increase in applied power results in a sharp increase in junction resistance. Analysis of the experimental data led us to the conclusion that AlN$_x$ tunnel barrier formation is a complex combination of nitrogen implantation and subsequent diffusion of nitrogen, facilitated by plasma heating. In addition, despite different conditions of tunnel barrier formation in different experiments, there is a unique dependence of sub-gap leakage current versus transitivity of the tunnel barrier.

References


Conclusions

Pushing the operation of SIS mixers towards THz frequencies requires strip-lines made of superconductors with higher Tc compare to Nb and high quality SIS junctions with lower R, values and/or higher gap voltage compare to the Nb/Al-AlOx/Nb junctions. Metal nitrides are frequently used in technologies aimed to reach this goal. Therefore a broad spectrum of metal nitrides deposited by various glow discharge based systems is examined in this thesis. The beginning of this thesis is dedicated to an empirical selection of film material, glow discharge type, substrate-target distance, and substrate material. Films of NbN, (Nb,Ti)N, and (Nb,Zr)N deposited by reactive magnetron sputtering on glass, Si, sapphire, and MgO wafers are compared in terms of intrinsic stress, transition temperature, and resistivity. XRD analysis revealed that all films have rock-salt cubic structure. The best results for all types of wafers are observed for (Nb,Ti)N films sputtered from a NbTi alloy target with 30 at. % Ti. (Nb,Ti)N films deposited on Si, sapphire, and glass wafers show a considerable degradation of Tc with film thickness due to poor crystallinity of the bottom layers of the films. Utilization of MgO wafers allows to produce epitaxial (Nb,Ti)N and NbN films with improved properties and better homogeneity. While utilization of the RF-sputtered MgO under-layers results only in resistivity reduction. Since DC and RF discharges produce films with similar Tc's and resistivities, DC discharge is selected for film deposition because it produces films with lower intrinsic stress. Maximum substrate-target distance is selected for film sputtering, because it provides the best uniformity and reduction of substrate-target distance does not improve the film properties.

The next step of the research is an examination of structural and electrical properties of (Nb,Ti)N films over a wide range of sputtering pressures. Nitrogen injection is optimized for each sputtering pressure to produce stoichiometric composition. TEM analysis revealed that the films consist of 20-40 nm grains. A change of the film structure from the Z1 structural zone to the ZT structural zone is observed as the sputtering pressure decreases. Tc has a moderate dependence on the sputtering pressure, while film resistivity increases one order of magnitude as the pressure increases. Because all of the films have RRR resistance ratios in the vicinity of unity, it is concluded that the origin of high resistivities is related to crystal imperfections. In particular, film resistivity is determined by vacancies in the ZT structural zone, while the voids on the grain boundaries and vacancies together determine the resistivity in the Z1 structural zone.

Accumulated knowledge about nitride growth enables to use the deposition of these materials as a tool for analysis of magnetron sputtering sources performance. A comparison between balanced and unbalanced sputtering sources is carried out on the
basics of monitoring the dependence of intrinsic stress, Tc, and resistivity of the films on sputtering pressure. No significant difference between the balanced and unbalanced sputtering sources has been found, since the properties of the (Nb,Ti)N obtained from unbalanced sputtering source are equivalent to the properties of the (Nb,Ti)N films obtained from the balanced one under lower sputtering pressures.

An evaluation of the NbN and (Nb,Ti)N film properties enables to conclude that the substrate surface temperature is not stable throughout the target lifetime. The unbalanced sputtering source shows a change in (Nb,Ti)N film properties equivalent to a decrease in the sputtering pressure, while the balanced sputtering source shows the opposite behavior. Furthermore, using an unbalanced source together with a grounded substrate table, it is possible to choose deposition conditions which yield stable and reproducible (Nb,Ti)N film properties throughout the target lifetime.

Understanding and proper characterization of the texture formation in (Nb,Ti)N films is very important since this process is driven by pseudo-morphic forces which depend strongly on the growth conditions. Variation of the sputtering pressure for different substrate-target distances have revealed that, increase in the adatom energy results in a change of texture from (111) to (100) for a constant chemical composition. However the process of texture formation is not exclusively kinetically limited. Despite that an increase in nitrogen injection results in an increase in the adatom energy, the system is driven towards (111) texture. TEM analysis shows that film texture is formed throughout the process of competitive growth. Despite the fact, that adatom energy and film chemical composition are the factors of different origin, film texture evolution is the same. A transition from (111) to (100) texture occurs via the abundance of (1γγ) textures, where 0≤γ≤1.

Since NbN has higher gap voltage compare to Nb this material has been tried as an electrode material for NbN/AlN/NbN tunnel junctions to produce the junction with higher gap voltage. The electrodes consisting of the stress free NbN films with Tc = 14.7 K are used. The junction try-layer is successfully obtained by DC magnetron sputtering without intentional substrate heating. The proximity effect and pinholes in the tunnel barrier cause marginal junction quality. Low Tc of bottom layers of a top junction electrode determines proximity effect. While sharp peaks on a surface of a bottom electrode cause pinholes in a tunnel barrier, since they have a height 2-3 times exceeding the thickness of AlN tunnel barrier.

The production of high quality Nb/Al-AlN/Nb tunnel junctions with low RnA values is characterized in the last chapter of this thesis. The goal of high quality junctions with low RnA values has been reached by substitution of the oxidation of Al layer by RF-glow discharge nitridation in the atmosphere of nitrogen. Locating the substrate on the electrode parallel to the driven electrode allows achieving a very mild bombardment of the substrate surface by nitrogen ions accelerated by the plasma potential. Analysis of the experimental data indicates that AlN tunnel barrier formation is a complex combination of nitrogen implantation and subsequent diffusion of nitrogen, facilitated by plasma heating.
Samenvatting

De ontwikkeling van SIS mixers voor de detectie van THz straling vereist niet allen hoge kwaliteit SIS junctions met een grotere gapenergie en/of kleinere $R_nA$ waarden dan conventionele Nb/Al-AlOx/Nb junctions, maar ook strip-lines van een supergeleidend materiaal met een hogere $T_c$ dan Nb. In dit proefschrift worden de eigenschappen beschreven van verschillende metaalnitride films gedeponeerd met verschillende op glimontlading gebaseerde technieken. Na de inleiding worden experimenten beschreven om te komen tot een optimale experimentele keuze van materiaal, substraat, ontladingsoort, afstand tussen substraat en target. Dunne lagen van NbN, (Nb,Ti)N, (Nb,Zr)N met behulp van magnetron sputtering gedeponeerd op glas, Si, saffier en MgO substraten worden vergeleken op grond van weerstand, transitietemperatuur en stress. XRD analyse toont dat alle lagen de NaCl structuur hebben. Voor alle soorten substraten werden de beste waarden waargenomen voor (Nb,Ti)N lagen gesputterd met een Nb$_{0.7}$Ti$_{0.3}$ target. Dunne (Nb,Ti)N lagen gesputterd op Si, glas en saffier vertonen een sterke degradatie van $T_c$ met de dikte, veroorzaakt door de slechte kristallijniteit van het onderste deel van de laag. Het gebruik van MgO substraten maakt het mogelijk lagen van NbN en (Nb,Ti)N met verbeterde eigenschappen en homogeniteit te groeien. Het gebruik van RF-gesputterde MgO onderlagen leidt tot de vermindering van de weerstand van de lagen. Hoewel DC- en RF-ontladingen lagen produceren met dezelfde $T_c$ en weerstand, is voor DC-ontlading gekozen omdat dat leidt tot minder stress in de lagen. Voor een betere uniformiteit is de substraat-target afstand is maximaal gekozen. Vermindering van de substraat-target afstand liet geen verbetering van de andere eigenschappen van de lagen zien.

De tweede stap van het onderzoek is de verkenning van de elektrische en structurele eigenschappen van (Nb,Ti)N lagen als functie van de sputterdruk. Stikstofdruk is geoptimaliseerd om de stoichiometrische compositie te produceren. TEM analyse toont dat de lagen uit 20-40 nm grote korrels bestaan. Als de sputterdruk lager wordt, verandert de lagenstructuur van de Z1 structuurzone naar de ZT structuurzone. $T_c$ is niet sterk afhankelijk van de structuur. Echter de weerstand daalt een orde van grootte. Aangezien alle lagen een RRR verhouding van ongeveer een hebben, kan worden geconcludeerd dat de oorsprong van de hoge filmweerstand te maken heeft met kristaldefecten. In het bijzonder, de weerstand wordt door vacatures bepaald in de ZT structuurzone, terwijl de weerstand in de Z1 structuurzone door vacatures en voids tussen korrels wordt bepaald.
Geaccumuleerde kennis over metaalnitrides maakt het mogelijk om de laaggroei te gebruiken als instrument om de sputterbronnen te onderzoeken. Een vergelijking tussen gebalanceerde en ongebalanceerde sputterbronnen is op grond van de sputterdruk afhankelijkheid van de stress, $T_\text{c}$, en weerstand. Er is geen duidelijk verschil tussen de gebalanceerde en de ongebalanceerde sputterbron gevonden, omdat de eigenschappen van (Nb,Ti)N lagen geproduceerd met de gebalanceerde sputterbron gelijk zijn aan de eigenschappen van (Nb,Ti)N lagen geproduceerd met de ongebalanceerde sputterbron bij hogere druk.

De evaluatie van de eigenschappen van NbN en (Nb,Ti)N leidt tot de conclusie dat de temperatuur van het substraatoppervlak niet constant is tijdens het leven van een target. Bij de ongebalanceerde sputterbron treedt een verandering van de eigenschappen van de lagen op, die equivalent is met een vermindering van de sputterdruk, terwijl bij de gebalanceerde sputterbron precies het omgekeerde optreedt. Echter, het gebruik van een ongebalanceerde sputterbron met een geaard substraat maakt het mogelijk om gedurende het leven van de target stabiele eigenschappen van de lagen te krijgen.

Begrip en de juiste karakterisering van de textuur in (Nb,Ti)N lagen zijn van groot belang, want de textuurformatie wordt door pseudomorfe krachten bepaald, die sterk afhankelijk zijn van de groeicondities. Uit de variatie van de sputterdruk voor verschillende substraat-target afstanden is gebleken, dat de toename van de adaatoom energie leidt tot een textuurverandering van (111) tot (100) bij constante scheikundige samenstelling. Echter, het proces van textuurformatie wordt niet alleen door de kinetiek beperkt. Ondanks het feit, dat vergroting van stikstofinjectie leidt tot een vergroting van de adatoomenergie, wordt het systeem naar een (111) textuur gedreven. TEM analyse laat zien, dat de textuur van de lagen wordt bepaald door het proces van competitive columnar growth. Hoewel de energie van adatomen en de scheikundige samenstelling factoren van verschillende oorsprong zijn, is de evolutie van de textuur hetzelfde. De transitie van (100) naar (111) textuur voltrekt zich via een verzameling (1γγ) texturen met $0 \leq \gamma \leq 1$.

Omdat in vergelijking met Nb, NbN een hoger gapenergie heeft, is dat materiaal als elektrode van NbN/AlN/NbN tunneljuncties getest om vjuncties met een hogere gapvoltage te fabriceren. De elektroden worden gemaakt van stressvrije NbN lagen met een $T_\text{c}$=14.7K. De junctie tri-layer werd met behulp van DC-sputtering zonder extra opwarming gegroeid. Dit proces leidt tot juncties met een middelmatige kwaliteit, die wordt veroorzaakt door het proximity effect en gaten in de tunnel barrière. Het proximity effect wordt veroorzaakt door een lage $T_\text{c}$ van de onderkant van de bovenelektrode. Scherpe pieken op het oppervlak van de onderste elektrode met een hoogte, die 2-3 keer groter is dan de dikte van de AlN isolator laag, veroorzaken de gaten in de tunnel barrière.

De fabricage van hoge kwaliteit Nb/Al-AlN/Nb tunneljuncties wordt in het laatste hoofdstuk van dit proefschrift beschreven. Het doel om hoge kwaliteit SIS juncties met lage $R\alpha$A waarden te maken wordt bereikt door de Al oxidatie te vervangen door RF-glimontladingsnitridatie. De positionering van het substraat evenwijdig met de aangedreven elektrode maakt een erg mild bombardement van het substraatoppervlak met
stikstofionen versneld door de plasmapotentiaal mogelijk. Analyse van de experimentele resultaten toont dat de formatie van de AlN tunnel barrière een complex proces is, dat bestaat uit een combinatie van stikstofimplantatie met daaropvolgend diffusie van stikstoef vergemakkelijk door plasma opwarming.
List of publications

This thesis is based on the following publications:


9. N. N. Iosad, A. B. Ermakov, F. E. Meijer, B. D. Jackson, T. M. Klapwijk, “Characterization of fabrication process of Nb/Al-AlN/Nb tunnel junctions with low $R_{\pi}A$ values up to 1 $\Omega \cdot \mu m^2$” *Superconductor Science Technology*, vol. 15, p. 945, June 2002.


**Related publications**


Acknowledgements

The work described in this thesis is a result of technological research carried out in three institutions. I began the research in the University of Groningen as Ubbo Emmius bursaal. The final stage of the work took place at Delft University of Technology. The technological facility of the Institute of Radio-Engineering and Electronics in Moscow was being used as well during the entire period of my thesis work.

First of all I want to acknowledge my supervisor Prof. T. M. Klapwijk for his tolerance and patience. I have enjoyed a lot a freedom in choosing the research topics myself. I had a remarkable opportunity to steer my "ship" myself and learn through my own mistakes. The second person to be acknowledged is Valery Koshelets, my scientific "godfather." He has played a crucial role in launching me on the right orbit. Although, it is necessary to mention the entire team of laboratory nr. 235, that contributed to my scientific growth, especially Lyudmila Filippenko. Ernest Kov’ev and Vladimir Roddatis from the Institute of Crystallography of RAS and Sergey Pokyakov from Moscow State University helped me a lot with the material science aspects of my thesis. During my work in Groningen I had a lot of fruitful discussions and productive collaboration with the groups of Prof. J. Th. M. De Hosson and Prof. D. O. Boerma. Persons of these groups, I want to acknowledge in particular, are Paul Bronsveld, Andrey Mijiristkii, and Sergey Grachev.

A lot of researchers at Delft Technical University assisted me in research as well. Niek van der Pers and Rob Delhez from the laboratory of the material science contributed as X-Ray experts. I am very thankful to the DIMES-Nanofacility team under the supervision of Dr. E. van de Drift. Their contribution to my thesis is immeasurable, just because it will not be possible to carry the research out without the facility developed and maintained by them. I want to acknowledge Ad Verbruggen from the department of applied physics for fruitful discussions in the field of material science.

This work was carried out in a close collaboration with the Space Research Organization of Netherlands. I had great pleasure to work together with Willem Luinge, Brian Jackson, and Gert de Lange.

In conclusion I want to acknowledge all people that are not mentioned above, but also made "invisible" contribution to my work: engineers, technicians, managers of all institutions that I have worked in.
Curriculum Vitae

5-October-1972

1989-1995

1993-Present

June 1995-
August 1995

February 1996-
August 1996

November 1996-
September 1999

October 1999
March 2002

Born in Moscow, Russia.

M. Sci. in Physics, Moscow State University, Russia.

Researcher at the Institute of Radio-Engineering and Electronics, Moscow, Russia.

Invited researcher at the Institut für Schicht und Ionentechnik, Forschungszentrum, KFA, Jülich, Germany

Invited researcher at the Department of Microelectronics at the Chalmers University of Technology, Göteborg, Sweden.

Ph. D. Research at the University of Groningen in the group of Prof. Klapwijk.

Ph. D. research at the Delft University of Technology in the group of Prof. Klapwijk.