ISSN 1330–0008
CODEN FIZAE4

INVESTIGATION OF REACTIVELY SPUTTERED NbN FILMS

IVAN HOTOVY, JOZEF BRCKA and JOZEF HURAN*

Department of Microelectronics, Slovak Technical University, Ilkovicova 3, 812 19 Bratislava, Slovakia
**Institute of Electrical Engineering, Slovak Academy of Sciences, Dubravska 9, 842 39 Bratislava, Slovakia*

Received 7 April 1995

Revised manuscript received 11 June 1995

UDC 538.975

PACS 68.55.Jk, 81.15.Cd

We have investigated the structural properties of thin films of reactively magnetron sputtered niobium nitride (NbN) under high–temperature annealing (with annealing temperatures ranging 850 to 950 °C) and with different nitrogen contents in the working gas mixture. Prepared NbN films were characterized by Auger electron spectroscopy (AES) and X–ray diffraction (XRD). The influence of rapid thermal annealing (RTA) on a change of the structure properties and surface morphology was investigated. The correlation between technological parameters and film properties, structure and composition were established.

1. Introduction

Refractory metals and their nitride compounds (NbN, TiN) of low electrical resistivity have a significant role in microelectronics and sensors, and also in micromechanics and superconducting electronics [1,2], because of their useful mechanical and electrical properties. They exhibit high hardness and good thermal stability up to 1000 °C. Despite the fact that NbN has been considered for use in

SIS (semiconductor-insulator-semiconductor junction device applications [3]), little is known about the dependence of the reactively sputtered film properties on deposition parameters and thermal annealing.

Reactive magnetron deposition can be used for NbN deposition, but it is a complex process, the kinetics of which occurs in several stages: transport of gas into the reaction zone [4], conversion of molecules into active states (ionisation, dissociation, excitation, etc. [5]), transport of active particles towards the surfaces (target, substrate and chamber walls), their interaction with surfaces [6] and the removal by pumping from the chamber of the resultant products. The process itself and thin film properties will be affected then by each of these stages. Moreover, the overall process is reactive (reactive gas is nitrogen, inert gas is argon), and thus to a great extent non–linear, showing hysteresis in the process parameters. Thus the gas flow conditions and final composition of the gas mixture can play a significant role in these processes.

In this paper, we report on the investigations of the structural properties and composition of niobium nitride (NbN) thin films as a function of nitrogen content in working gas mixture and high annealing temperatures. Auger electron spectroscopy (AES) and X–ray diffraction (XRD) were employed to study the structural properties of these films.

2. *Experimental procedure*

The NbN films were deposited by dc reactive magnetron sputtering from a Nb target (50.8 mm in diameter, thickness of 6 mm, nominally 99.95% pure) in a

TABLE 1.
Sets of parameters used to investigate the film properties.

Sample	H4	H5	H6	H7	H8	H9
Nitrogen content in working gas [%]	0	2	5	10	15	20
Nitrogen flow [sccm]	0	1.6	4.0	8.0	12.0	16.0
Total presure [Pa]	0.5	0.5	0.5	0.5	0.5	0.5
d.c. discharge power [W]	300	300	300	300	300	300
Target to substrat spacing [mm]	75	75	75	75	75	75
Thickness after deposition [nm]	120	115	115	120	115	110

mixture of nitrogen (99.999% pure) and argon (99.999% pure) onto unheated, semi–insulating GaAs and SiO_2/Si substrates. The conditions of deposition are given in Table 1. Nitrogen content in the gas mixture, defined as the ratio of the nitrogen flow to the total flow (nitrogen flow and argon flow) varied from 0% to 20% . The

films were annealed by rapid thermal annealing in vacuum at temperatures of 800, 850 and 950 °C for 10 seconds. Composition of the films were analyzed with Auger electron spectroscopy (AES). The crystal structure of the films was identified with X–ray diffraction (XRD) in the Bragg-Brentano geometry. Samples were measured in the range $2\theta = 32° - 62°$ with steps $2\theta = 0.04°$ and time of measurement for each step was 5 s.

3. Results and discussion

3.1. Composition analysis

Elemental composition of the films versus the nitrogen content is shown in Fig. 1. From our results, we can suppose that the content of nitrogen in a film depends on the amount of nitrogen in the working gas mixture. At a small content of nitrogen (up to 5%), the changes in the content of nitrogen which is incorporated in the film, are expressive. In this range we found that the nitrogen content in the film was nearly proportional to the nitrogen content in Ar-N_2 mixture. In Fig. 1 one can also observe that when the amount of nitrogen in the sputtering gas exceeds about 10%, a saturated value of nitrogen in the film is approached. The content of oxygen in the films prepared is almost constant, and its value was up to 2 at % . However, the content of carbon increases linearly with increasing concentration of nitrogen in the working gas, and the source of carbon can be CO_2 desorbed from the walls of the vacuum chamber during deposition or oil backstreaming from the forepump.

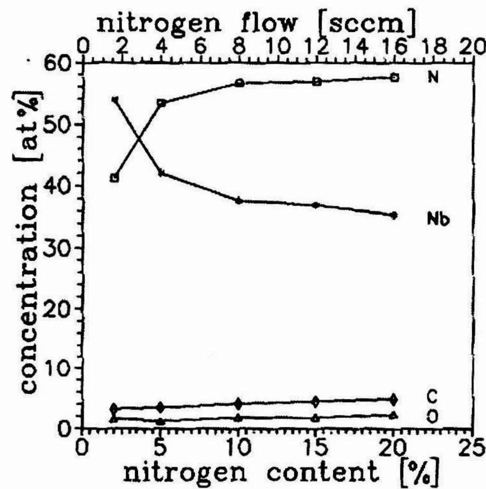

Fig. 1. Chemical composition investigated by AES of the NbN *layers prepared at the various nitrogen contents (or nitrogen flow) in a gas mixture. The total pressure was 0.5* Pa *and discharge power was 300* W.

3.2. Structural analysis

Figures 2 and 3 present the diffraction patterns of the samples which were prepared with different nitrogen contents in the working gas, in the range of 2θ where the diffraction peaks were observed. From the XRD spectra of NbN films as–deposited, it was found that the NbN films prepared have both amorphous or polycrystalline structure. In the diffraction patterns from the as–deposited samples with 2, 5 and 20% nitrogen content (Fig. 2) only the GaAs diffraction peaks from the substrate are seen, indicating the amorphous nature of these as–deposited NbN layers. The diffraction patterns from others samples, prepared at 10 and 15% nitrogen content, show the presence of the (fcc) NbN phase (Fig. 2). From the calculated values of the lattice parameter, we found that their values increased with increasing of the nitrogen content in the layer. According to Toth et al. [7] the (fcc) NbN phase is sensitive on the ratio of Nb/N, and with this the lattice parameter changes systematically. Our calculated values are higher than the standard value for the NbN phase (0.4395 nm). We explain this increase by the fact that prepared films contain a lot of nitrogen (in accordance with the AES measurement, it was 56.6 at % resp. 56.9 at %) which can be situated in interstitial positions and can cause the expansion of the lattice. It has been observed by Thakoor et al. [8] that the inclusion of carbon in NbN, introduced primarily to stabilize this NbN phase, also increases the lattice constant.

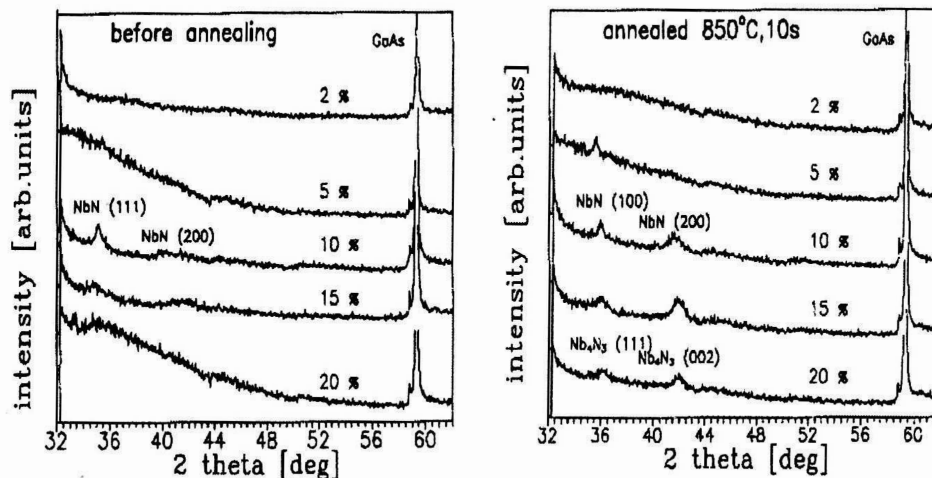

Fig. 2. XRD spectra from the as-deposited NbN *films prepared at various nitrogen contents in the working gas. Substrate material was semiinsulating* GaAs.

Fig. 3. XRD spectra from previous NbN *films (Fig. 2) annealed at 850* °C *for 10 seconds (right).*

The effect of the annealing temperature of 850 °C on the structure of films is the following (Fig. 3). The sample prepared with a 2% nitrogen content becomes

amorphous. The structure of the sample formed with 5% changes from amorphous to (fcc) NbN phase. With the nitrogen content of 10% , the structure is conserved but the lattice parameter decreased substantially (to 0.437 nm) what could mean a decrease of the nitrogen content in the film. At the two last samples (15 and 20% nitrogen content) we suppose that the films transform into the tetragonal Nb_4N_3 phase, because the diffraction peaks better correspond to this phase. Our conclusion is confirmed by the results of Thakoor et al. [8] who observed the tetragonal Nb_4N_3 phase in the sample prepared at the high partial pressure of nitrogen, too. It is possible that during annealing, the interstitial nitrogen is removed from the lattice which is consequently distorted into tetragonal phase because these samples were prepared at the high nitrogen content and the lattice parameter as–deposited was large (0.499 nm).

We observed that with increasing annealing temperature, the structure of the NbN film, formed with 5% nitrogen content, is not changed, although the lattice parameter is decreased from 0.441 nm at 800 °C, to 0.440 nm at 900 °C and finally to 0.437 nm at 950 °C. This contention is in agreement with the fact that increasing of annealing temperature causes a loss of nitrogen atoms from the NbN crystalline lattice. The lattice parameter of the sample annealed at 900 °C has exactly the same value as the (fcc) NbN phase.

4. *Conclusion*

In this investigation, we have shown that by varying the nitrogen content in working gas in reactive magnetron sputtering, it is possible to find and control the properties of niobium nitride thin films. We have found that the nitrogen content in the growing film depends on the nitrogen content in the working gas, however above 10% of nitrogen in the gas its content in the film increases only slightly. We have also shown by X–ray diffraction that NbN films prepared both at the lowest (2 and 5 %) and the highest (20 %) concentrations in the gas have amorphous structure. The others films showed the (fcc) NbN phase with the $< 111 >$ line dominant and a weaker $< 200 >$ line present. The results from AES and XRD analysis were compared and they indicated that the films with optimal properties can be grown with the 10% nitrogen content. These films had the (fcc) NbN structure.

References

1) M. S. Wong, W. D. Sproul, X. Chu and A. Barnett, Jour. of Vac. Sci. and Technol. **A11** (1993) 1528;

2) M. J. Deen, Thin Solid Films **152** (1987) 535;

3) W. N. Maung, D. P. Butler and Ch. L. Huang, Jour. of Vac. Sci. and Technol. **A11** (1993) 615;

4) T. Larsson, H. O. Blom, C. Nender and S. Berg, Jour. of Vac. Sci. and Technol. **A6** (1988) 1832;

5) D. K. Hohnke, D. J. Schmatz and M. D. Hurley, Thin Solid Films **118** (1984) 301;
6) S. Kadlec, J. Musil and J. Vyskocil, Jour. of Vac. Sci. and Technol. **A8** (1990) 1560;
7) L. E. Toth, *Transition Metal Carbides and Nitrides*, Academic Press, New York, 1971;
8) S. Thakoor, J. L. Lamb, A. P. Thakoor and S. K. Khanna, J. Appl. Phys. **58** (1985) 4643.

ISTRAŽIVANJE REAKTIVNO NANEŠENIH NbN SLOJEVA

Istraživana su strukturna svojstva tankih slojeva niobium nitrida (NbN) reaktivno-raspršenih magnetronom, uz visoko-temperaturno otpuštanje (na 850 do 950 °C), s različitim sadržajima dušika u radnom plinu. Dobiveni NbN tanki slojevi istraženi su Augerovom elektronskom spektroskopijom (AES) i rendgenskom difrakcijom (XRD). Proučavan je utjecaj brzog toplinskog otpuštanja na strukturna svojstva i površinu slojeva.