PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. 3 No 1, 01NTF17(3pp) (2014)

Structural and Mechanical Properties of Nanocomposite Nb-Al-N Films

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(Received 08 July 2014; published online 29 August 2014)

Nb-Al-N films were deposited by magnetron sputtering of the Nb and Al targets in the Ar-N_2 atmosphere on silicon wafers at various currents supplied to the magnetron device with the Al target (I_{Al}=100, 150, 200, 300 mA). The films were studied with XRD, FTIR spectroscopy, as well by nanoindentation and Knoop indentation tests. The films were found to have the nanocomposite nc-B1-NbN_x/a-AlN structure and exhibit the nanohardness and Knoop hardness in the ranges of 29-33.5 GPa and 46-48 GPa, respectively. The hardness and elastic modulus has an extreme dependence on I_{Al}

Keywords: Nb-Al-N films; AlN films; Magnetron sputtering; Film structure; Mechanical properties; Nanoindentation.

PACS numbers: 81.15.Cd62.20.Qp

1. INTRODUCTION

NbN-based films exhibit a variety of interesting properties like high hardness and electrical conductivity, thermal stability and chemical inertness [1]. NbN films are used as cathode material for field emission in vacuum microelectronic devices [2]. Nanolayered coatings based on NbN such as TiN/NbN, CrN/NbN, Mo/NbN and W/NbN have been found to show improved mechanical properties as compared to monolayer coatings [2]. Nb-Al-N films were prepared by using various deposition procedures [3-7]. It was shown that the incorporation of Al atoms into the crystal lattice led to the formation of solid solution $Nb_{1-x}Al_xN$. For $Nb_{1-x}Al_xN$ coatings, the B1 structure was preferable with x below 0.45. In the range of x=0.45-0.71, a mixed B1 and B4 structure was observed, whereas for x>0.71, a B4 structure formed [6,7]. So, the deposited Nb-Al-N films consisted of $Nb_{1-x}Al_xN$ solid solutions with the B1, (seldom B_k) and B4 structures, or their mixtures [3-7]. On the other hand, so far, nanocomposite NbN/AlN films were not prepared. Therefore, in the present investigation, we aimed at to deposit nanocomposite Nb-Al-N films on the assumption that the nanocomposite films should exhibit improved mechanical properties as compared to those of $Nb_{1-x}Al_xN$ films.

In the present work, Nb-Al-N films were deposited by magnetron sputtering of the Nb and Al targets at different currents supplied to the magnetron devices with the Al target (I_{Al}). The structural and mechanical properties are analyzed depending on values of I_{Al}.

2. EXPERIMENTAL DETALIES

Nb-Al-N films were deposited on the mirror-polished Si (100) wafer by DC magnetron sputtering the Nb (99.9%, Ø72×4 mm) and Nb (99.999%, Ø72×4 mm) targets in an argon-nitrogen atmosphere at the following deposition parameters: substrate temperature T_S= 350 ^{0}C; substrate bias U_B =-50 V; flow rate (F) F_{Ar}=40 sccm; F_{N2}=13 sccm; working pressure P_C=0.17 Pa. The current applied to the Al target (I_{Al}) was 100, 150, 200 and 300 mA, which corresponded to a discharge power density P_{Al}= 5.7, 8.6, 11.4, and 17.1 W/cm^2, respectively. The current on the Nb target (I_{Nb}) was 300 mA (P_{Nb}=17.1 W/cm^2). The base pressure of the vacuum chamber was better than 10^{-4} Pa. The distance between the targets and the substrate holder was 8 cm. The dihedral angle between the target planes was ~ 45^0. The substrates were cleaned ultrasonically before they were put into the vacuum chamber. Also, before deposition, the substrates were etched in the vacuum chamber in hydrogen plasma during 5 min.

The crystal structure of the films was determined by X-ray diffraction (XRD, diffractometer DRON-3M) using CuK_α radiation. The crystallite size in films was evaluated from the broadening of peaks in X-ray diffraction spectra using Scherrer formula. The Fourier transform infrared (FTIR) spectra were measured at room temperature in the range of 400 – 4000 cm^{-1} by a spectrometer "FSM 1202" LLC «Infraspek». The hardness and elastic modulus of films were determined from indentation by Nanoindenter-G200 instrument equipped with a Berkovich pyramidal tip under load in the range of 9-13 mN. This range of loads was chosen in order to obtain prominent plastic deformation of film while avoiding the influence of substrate material. The nanohardness (H) and elastic modulus (E) data was obtained from the load-displacement curves using the Oliver and Pharr method. The Knoop hardness (HK) was estimated by a Microhardness Tester Micromet 2103 BUEHLER LTD at loading of 100 mN. The thickness of the films was determined with an optical profilometer "Micron-Gamma". The thickness of Nb-Al-N films (d) weakly depends on I_{Al}. The values of d was in the range of 0.7-0.9 μm.

3. RESULTS AND DISCUSSION

In Fig. 1 we show the XRD spectra of the Nb-Al-N films deposited at different I_{Al}. Two peaks at 2Θ ~ 35.4-36.0° and 2Θ ~ 41.1-41.2° are identified as the B1-NbN(111) (35.4°) and B1-NbN(200) (35.1°) reflections, respectively [038-1155]. A comprehensive analysis shows that the positions of the XRD peaks weakly depend on I_{Al}, except those for the film deposited at the highest discharge power at the Al target. For this film, 2Θ = 36° and 2Θ ~ 41.2° for B1-NbN(111) and B1-NbN(200) reflections, respectively, which indicates the formation $Nb_{1-x}Al_xN$ solid solution. For the sake of comparison, one reminds that the lattice parameters for B1-NbN and B1-AlN are a=4.393 Å and 4.12 Å, respectively [5]. So, the substitution of Nb with Al should lead to shifting the XRD peaks towards high angles, which takes place in the XRD spectrum of the last film.

The average grain size (D) of the films as a function of I_{Al} is shown in Fig. 2. One can see that the films are nanostructured with the average grain size in the range of 10-21 nm. The value of D reaches a minimum value for the film deposited at I_{Al} = 200 mA.

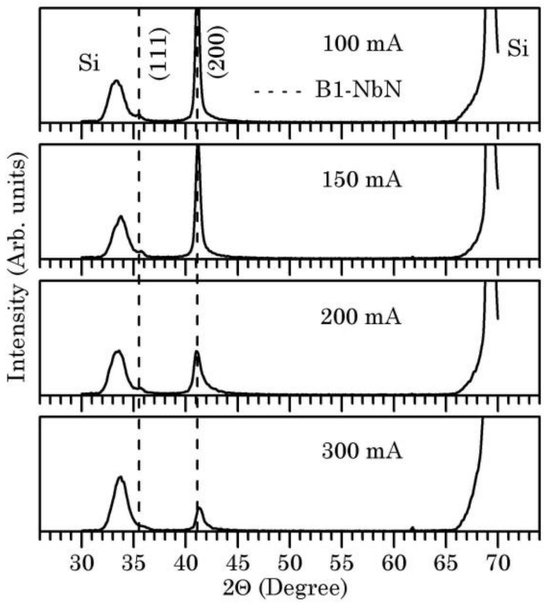

Fig. 1 – XRD spectra of the Nb-Al-N films deposited at various I_{Al}.

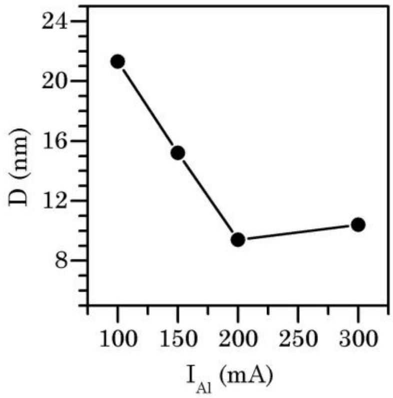

Fig. 2 – Average grain size of Nb-Al-N films as a function of I_{Al}.

We have deposited AlN films varying I_{Al}. The XRD investigations showed that all AlN films were amorphous (a-AlN) (not shown here). The FTIR spectra of AlN films are shown in Fig. 3. The Al-N network is improved with increasing I_{Al}: the band at 667 cm^{-1}, associated with the Al-N vibrations [8], becomes more prominent.

Comparing the results presented in Figs 1-3, we aim at a conclusion that the nanocomposite nc-B1-NbN_x/a-AlN films form at moderate currents 100 ≤ I_{Al} ≤ 200 mA. The nanocomposite films represent an aggregation of the B1-NbN_x crystallites embedded into amorphous AlN matrix. The film deposited at I_{Al} > 200 mA, consist of a $Nb_{1-x}Al_xN$ solid solution with the cubic structure.

The results of nanoindentation and microindentation of the deposited films are presented in Figs. 4 and 5. It is seen that the nanohardness (H), Knoop hardness (HK) and elastic modulus (E) of Nb-Al-N films are higher than those of NbN and AlN films. Also, the mechanical characteristics of the nanocomposite films are better compared to those of the $Nb_{1-x}Al_xN$ film. We note that Knoop hardness is higher than nanohardness by ~ 50%. This circumstance can be assigned to the fact that nanoindentation occurs at a dynamical regime, whereas, Knoop hardhess is determined at a static regime.

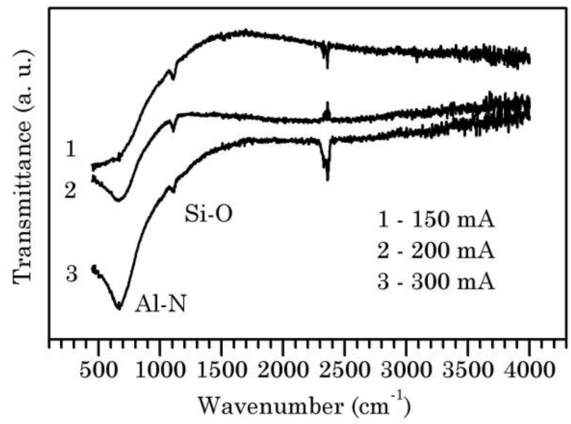

Fig. 3 – FTIR spectra of the AlN films deposited at various I_{Al}.

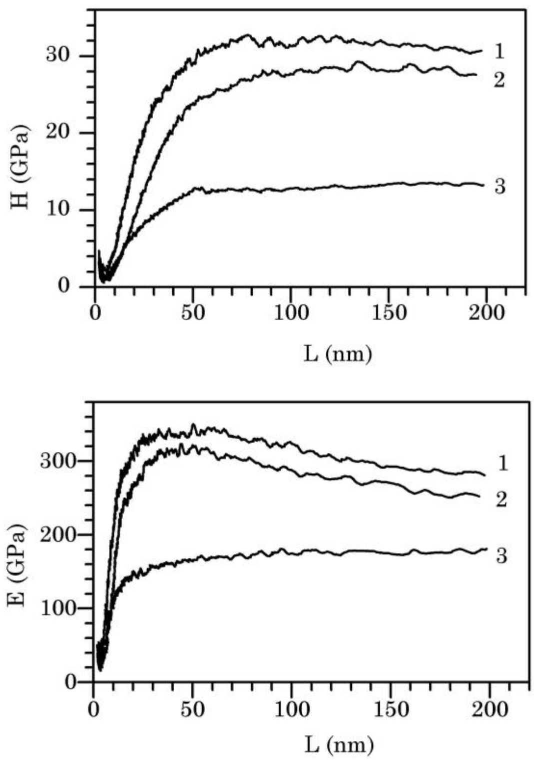

Fig. 4 – Nanordness (H) and elastic modulus (E) of the nanocomposite film deposited at I_{Al} = 200 mA (1) in comparison with those of NbN (2) and AlN (3) films, deposited at I_{Nb} =300 mA and I_{Al} = 200 mA, respectively. The values are presented as functions of indenter penetration.

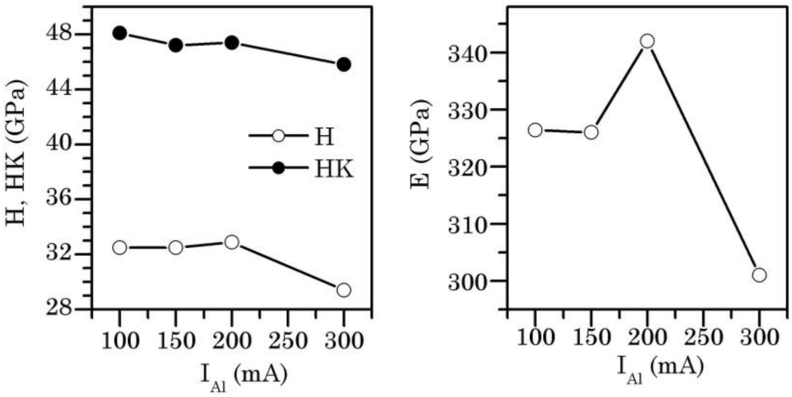

Fig. 5 – Nanohardness (H), Knoop hardness (HK) and elastic modulus (E) as functions of I_{Al}.

4. CONCLUSIONS

Nb-Al-N films were deposited by magnetron sputtering the Nb and Al targets at various currents supplied to the magnetron device with the Al target (I_{Al}). The films were characterized by XRD, FTIR spectroscopies, as well by means of nano- and micro-indentations. It was found that the nanocomposite nc-B1-NbN_x/a-AlN films formed at moderate currents 100 $\le I_{Al} \le$ 200 mA. At $I_{Al} >$ 200 mA, the film consisted of a $Nb_{1-x}Al_xN$ solid solution with the cubic nanostructure. The nanocomposite coating with the grain size of ~ 10 nm exhibits highest values of H and E. Taking into account the mechanical properties of the deposited nanocomposite films, they can be recommended as wear-resistant and protective coatings.

REFERENCES

1. S.A. Barnett, A. Madan, I. Kom, K. Martin, *MRS BULLETIN, Murch*, 169 (2003).
2. Y. Gotoh,M. Nagao, T. Ura,H. Tsuji, J. Ishikawa, *Nucl. Instr. Methods Phys. Res. B* **148**, 925 (1999).
3. T.I. Selinder, D.J Miller, K.E. Gray, Vacuu, **46**, 1401 (1995).
4. Y. Makino, K. Saito, Y. Murakami, K. Asami, *Solid State phenomena* **127**, 195 (2007).
5. H. C. Barshilla, B. Deepthi, K.s. Rajam, *J. Mater. Res.* **23**, 1258 (2008).
6. R. Franz, M. Lechthaler, C. Polzer, C. Mitterer, *Surf. Coat. Technol.* **204**, 2447 (2010).
7. D. Holec, R. Franz, P.H. Mayrhofer, C. Mitterer, *J. Phys. D* **41**, 145403 (2010).
8. K. Jadannadham, A.K. Sharma, Q. Wei, R. Kalyanraman, J. Narayan, *J. Vac. Sci. Technol. A* **16**, 2804 (1998).