Thermo Mechanical Characteristics of Niobium Oxide Optical Thin Films Deposited by Dual Ion Beam Sputtering

E. Çetinörgü, B. Baloukas, O. Zabeida, J.E. Klemberg-Sapieha, and L. Martinu,
École Polytechnique de Montréal, Québec, Canada

ABSTRACT

Advanced applications of optical thin films frequently require considering the mechanical and thermal properties of the applied high and low index materials. In the present work, the growth of niobium oxide thin films in a dual ion beam sputtering (DIBS) system were systematically studied, and their microstructure and properties were specifically related to the energetic conditions dictated by the energy and flux of the bombarding ions. Film properties such as internal stress, hardness, Young's modulus, thermal expansion coefficient, Poisson ratio, and adhesion were tested using substrate curvature method, depth-sensing indentation, and microscratch measurements. The refractive index, extinction coefficient, and optical transmission were determined using spectroscopic ellipsometry and spectrophotometry. The average hardness and Young's modulus of the deposited niobium oxide films increased from 5.5 to 6.5 GPa, and from 119 to 130 GPa, respectively, when increasing the secondary ion beam current from 100 to 150 mA. The Poisson ratio and the thermal expansion coefficient of the deposited films were 0.38 and 4.85×10^{-6} °C^{-1}, respectively. The internal stress of the niobium oxide films decreased from 220 MPa to ~100 MPa when the secondary ion beam energy increased from several tens of eV to 550 eV. We correlate this change in stress with the decrease of the refractive index from 2.32 to 2.26, (@ 550 nm).

INTRODUCTION

Metal oxide dielectric films are frequently used in a variety of applications such as, interference filters, photovoltaic solar cells, waveguides, and electrochromic devices. Niobium oxide (NbO_x where x =1.4-2) dielectric films have attracted much interest due to their optical properties: wide band gap (~3.85 eV), high index of refraction (~2.4), and low extinction coefficient (<10^{-4}) in the visible and near infrared spectra. Furthermore, NbO_x films are good candidates for many applications due to their superior chemical and thermal stability compared to other dielectric metal oxide materials. NbO_x dielectric films have been successfully prepared by various techniques including plasma enhanced chemical vapor deposition (PECVD) [1], atomic layer epitaxy [2], ion beam sputtering (IBS) [3,4], reactive magnetron sputtering [5,6] and spray deposition [7]. Among these methods, it has been shown that absorption-free films in the VIS and NIR spectra can be deposited using ion beam sputtering. Additionally, energetic particle bombardment has a significant effect on the properties of the deposited films such as grain size, defect levels, and the optical and mechanical characteristics. In dual ion-beam sputtering (DIBS) the target is sputtered by the primary ion source, while additional ion bombardment from the second ion beam ensures further densification [8]. In order to design and fabricate high quality thin films devices with high reliability, the effects of the deposition conditions on the characteristics such as optical constants, mechanical properties, and stress must be precisely determined [9]. In this content, the coefficient of thermal expansion (CTE), and the Poisson's ratio (ν) of NbO_x have not been determined, and the film users only rely on the limited data for the bulk crystalline material; This includes CTE =5.8×10^{-6} °C^{-1}[10] and ν=0.23 [11], or ν=0.19 [12].

In the present work, we systematically study the growth of NbO_x films using DIBS, particularly, the effect of second ion beam energy and ion beam current on the microstructure, and the optical and mechanical characteristics. We focus on the optimization of the deposition conditions to obtain high quality coatings with low stress, good adhesion, low absorption, and high refractive index, and we describe the methodology for the assessment of the CTE and ν values.

EXPERIMENTAL METHODOLOGY

NbO_x films have been deposited on glass, UV fused silica (UVFS), one side polished 50.8 mm diameter Si(100) and GaAs(100) substrates using the Spector® DIBS system at room temperature. The first ion beam source (16 cm- diameter) was used to sputter the Nb target using an ion energy (E_i) of 1250 eV and ion current (I_i) of 600 mA. The second source (12 cm-diameter) was used to modify the deposited layers properties while varying the ion beam energy and the ion beam current from 50 to 550 eV, and from 100 to 150 mA, respectively. The base chamber pressure was 2.6×10^{-7} torr, and the oxygen flow during the deposition was 28 sccm.

The optical characterization was performed using a variable angle spectroscopic ellipsometer (VASE, J.A. Woollam Co.). The optical transmission of all films was measured using a Perkin-Elmer Lambda 19 spectrophotometer. The optical properties were modeled using the Tauc-Lorentz (TL) disper-

51st Annual Technical Conference Proceedings, Chicago, IL, April 19–24, 2008 ISSN 0737-5921

sion formula for the refractive index, $n(\lambda)$, and the extinction coefficient, $k(\lambda)$. In addition to the optical constants, film thickness, d, was determined by the same fitting process.

Film hardness (H) and the reduced Young's modulus (E_r) of the coatings were obtained by depth-sensing nanoindentation using a Triboindenter instrument (Hysitron, Inc). The maximum and the minimum loads were in the range from 100 to 5000 μN. Twenty independent indentations per sample were repeated for each load.

Film adhesion evaluation was performed by using a microscratch tester (MST-CSEM), which is equipped with a Rockwell C diamond hemispherical tip (50 μm). The scratch length and the maximum load were 10 mm and 5N, respectively. The critical load (L_C), which is the minimum load at which coating damage can be observed, characterizes the mechanical resistance of the interface and/or of the coating. In the present work, we assumed that the critical load is the load in which we observed the film detachment.

Film stress (σ) was evaluated by measuring the sample curvature in a Flexus 2320 (Tencor) laser deflection system before and after deposition and using the Stoney equation [13]. The CTE and the ν values were derived using the two substrate method [14], utilizing the σ-T measurements performed in the 30-120°C and 30-240°C temperature ranges. Assuming that Young's modulus and CTE of the film are independent of temperature (T), the change of the stress as a function of T is given by the expression:

$$\frac{d\sigma}{dT} = \left[\frac{E}{(1-\nu)}\right]_{film} (\alpha_{sub} - \alpha_{film}) \quad (1)$$

where α_{sub} and α_{film} are the CTE values of the substrate and of the film, respectively, $E/(1-\nu)$ is the biaxial Young's modulus of the film, and $d\sigma/dT$ is the slope of the σ vs T relationship. If two substrates are used, the solution for the biaxial Young's modulus and CTE of the film can be presented as:

$$\left[\frac{E}{1-\nu}\right]_{film} = -\frac{\dfrac{d\sigma_1}{dT} - \dfrac{d\sigma_2}{dT}}{\alpha_1 - \alpha_2} \quad (2)$$

and

$$\alpha_{film} = \frac{\alpha_2 \dfrac{d\sigma_1}{dT} - \alpha_1 \dfrac{d\sigma_2}{dT}}{\dfrac{d\sigma_1}{dT} - \dfrac{d\sigma_2}{dT}} \quad (3)$$

where the indices "1" and "2" correspond to substrates "1" and "2". If the σ vs T plots are linear and the CTE's of the substrates are known, then the biaxial modulus and CTE for the film can be obtained from Eqs. (2) and (3). In the present work, the procedure of determining ν is based on measuring E_r using the nanoindentation technique [15]:

$$\frac{1}{E_r} = \frac{1-\nu_{film}^2}{E_{film}} + \frac{1-\nu_i^2}{E_i} \quad (4)$$

where, E_i and ν_i are the Young's modulus and Poisson's ratio of the indenter, and E_{film} and ν_{film} are the Young's modulus and Poisson's ratio of the film, respectively. E_r then used to calculate ν_{film}.

RESULTS AND DISCUSSION

The average transmission in the visible spectrum of all deposited films was 77% independent of the deposition conditions. The maximum optical transmission was equal to the substrate transmission, and did not depend on the ion energy, indicating that the deposited films were absorption free. However, lower transmission peaks were observed with films deposited without applying the secondary ion beam, compared to those observed in films deposited while the secondary ion beam was operating, indicating the presence of some weak absorption. In addition to the difference in the transmission peaks, a shift was of observed in the interference pattern of this two groups of films, indicating a decrease in film thickness correlated with the increased ion beam energy. Table 1 presents the optical constants of the deposited films and the deposition rates. Deposition rate decreased from 0.29 to 0.25 nm/s, as function of E_i and I_i.

Table 1: Optical constants of NbO_x films.

Deposition Conditions E_i I_i	n (550 nm)	k (550 nm)	Deposition Rate (nm/s)
No Assist	2.31	0.002	0.29
50 eV - 100 mA	2.31	$<10^{-5}$	0.27
250 eV - 100 mA	2.27	$<10^{-5}$	0.26
400 eV - 100 mA	2.27	$<10^{-5}$	0.25
550 eV - 100 mA	2.27	$<10^{-5}$	0.25
50 eV - 150 mA	2.32	$<10^{-5}$	0.27
250 eV - 150 mA	2.28	$<10^{-5}$	0.26
400 eV - 150 mA	2.27	$<10^{-5}$	0.25
550 eV - 150 mA	2.27	0.003	0.25

Figure 1 shows examples of the typical plots of the refractive index for highly dielectric films. The values of *n* for films deposited with ion assist (except 50 eV) were lower than those of films deposited without secondary ion beam assistance. The *n* of all films at 550 nm was in the range 2.26 to 2.32. The decrease in *n* with increasing E_i may be related to lower film density caused by the re-sputtering of condensed atoms. The values of *k* for films deposited at I_i=150 mA and E_i=550 eV and the films deposited without any ion beam assistance had some weak absorption, indicating low film quality. However, the other films were absorption free ($k<10^{-5}$) and highly transparent in VIS and NIR regions.

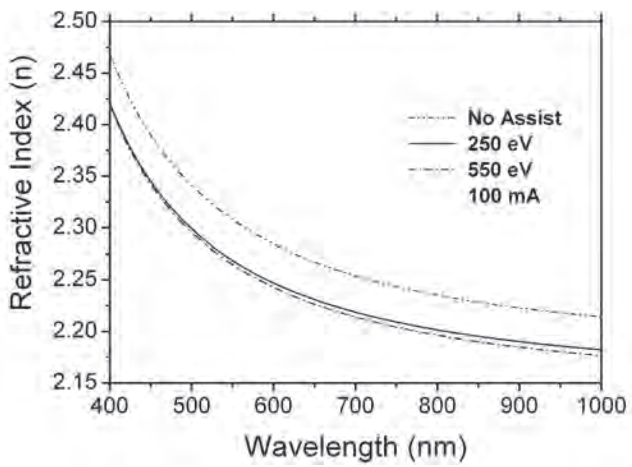

Figure 1: Refractive index dispersion of NbO_x for different ion beam energies.

The scratch measurements were performed using a 50 µm diameter stylus from 0 to 5N. The adhesion of the deposited films was then expressed in terms of L_C values. L_C of the films was in the range of 2.6-3.5 N, and 2.2-3.2 N for 100 mA and 150 mA ion beam currents, respectively, indicating good adherence. Although, the highest L_C was 3.5 N for films deposited at 400 eV and 100 mA, weak correlation was found between the L_C and the deposition conditions.

A typical load-displacement (*F*-*h*) curve for the deposited films is presented in Figure 2 in which the effects of the holding time and the loading rate on E_r and *H* are presented. The derived *H* and E_r values of the films are summarized in Table 2, and they appear to be only weakly affected by the secondary ion beam source. The average *H* and E_r of the films deposited at 100 mA were 5.7 and 122 GPa, whereas those of deposited at 150 mA were 6.3 and 127 GPa, respectively.

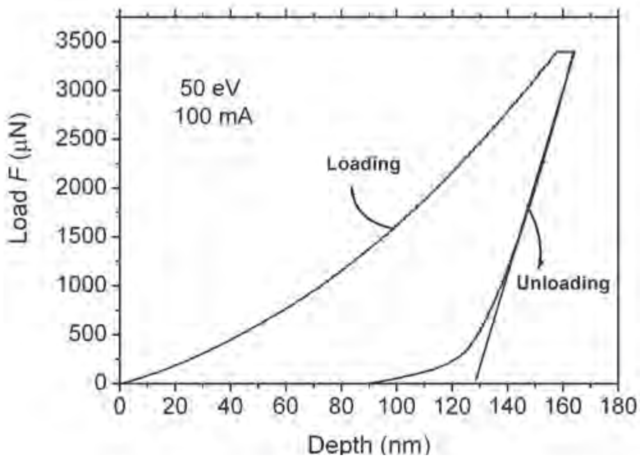

Figure 2: Typical load-displacement curve of NbO_x film deposited with 50 eV ion beam energy and 100 mA ion beam current.

Table 2: H and E_r as a function of the deposition conditions.

Deposition Conditions E_i I_i	Hardness (GPa)	Reduced Young's Modulus (GPa)
No Assist	5.7	119
50 eV - 100 mA	5.5	127
250 eV - 100 mA	5.9	125
400 eV - 100 mA	5.8	117
550 eV - 100 mA	5.6	118
50 eV - 150 mA	6.5	130
250 eV - 150 mA	6.4	128
400 eV - 150 mA	6.3	125
550 eV - 150 mA	5.9	123

Stress of the deposited films is presented in Figure 3 as a function of the ion beam parameters. The stress was compressive for all deposited films, and it decreased with increasing E_i from 220 MPa to 105 MPa, whereas it increased with I_i about 5%. Although, a large body of stress data has been compiled over the past fifty years, in general, there is no fully accepted model for stress evaluation and its dependence on the ion energy [16]. Recently, Davis [17] proposed a simple model to explain the formation of compressive stress in thin films with simultaneous bombardment by energetic ions or atoms. In this model, two processes take place: initially, the incoming atoms are incorporated in the growing film by a knock-on process of the energetic ions, generating stress in the film, as the implanted atoms are in metastable positions. At the same time, part of the energy of the implanted atoms is transferred to the neighboring atoms, leading to their release from their metastable positions due to thermal spikes, and thus giving rise to stress reduction. This mechanism can explain the present stress relaxation observed in this work at increased E_i, however, increasing the ion current increased the stress and decreased optical quality of the films.

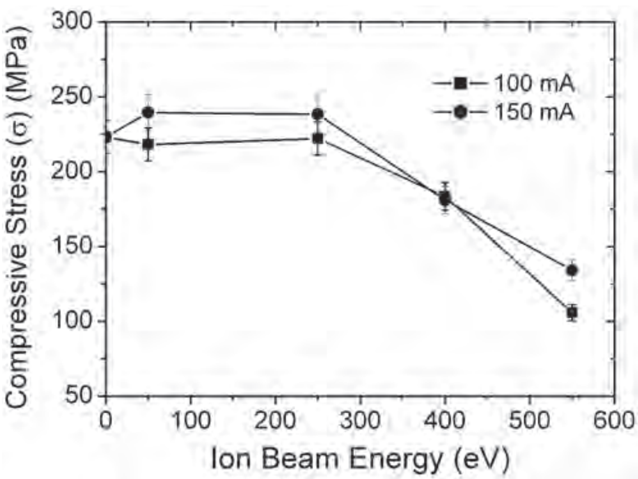

Figure 3: Stress behavior of NbO_x films as function of ion beam energy for different ion currents.

In Figure 4, typical σ–*T* plots of the heating and cooling cycles of films deposited at 400 eV and 100 mA on Si and GaAs substrates are presented. The dσ/d*T* slopes of the 30-120°C heating cycle were used to determine CTE and ν using Eqs. (2-4). The calculated values of ν and CTE are ~0.38 and ~4.85×10^{-6} °C^{-1}, respectively. The value of ν is higher than that obtained by Chudoba *et al*. (0.23) [11] and 0.19 by Samsonov [12], while the value of the CTE is lower than that measured by Dwivedi and Subbaro [10]: CTE=5.8×10^{-6} °C^{-1}. The error involved in the calculations begins to be significant when the determination of dσ/d*T* slopes can not be sufficiently accurate and/or the values of substrate CTE are not well known. Statistical analyses can be used to improve accuracy of the CTE and ν by determining the effects of error in each independent variable on the calculation. In our results, we found that the error in determination of the dσ/d*T* on both types of substrates caused a small error in CTE value (±0.09), however, the same analyses showed that the error in ν value for film deposited on GaAs substrate was higher (±0.5) than that of deposited on Si (±0.06). Additional study of these parameters is required to establish whether the differences between these data are significant.

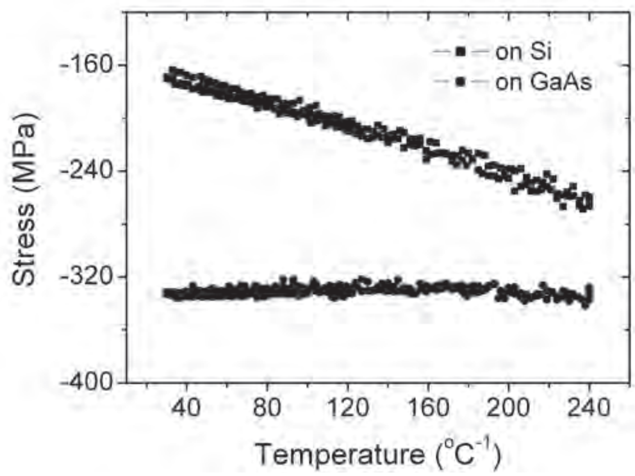

Figure 4: Stress-Temperature plots of NbO_x films deposited on Si and GaAs .

CONCLUSIONS

In the present work, the effects of the secondary ion beam energy (E_i), and the ion beam current (I_i) on the mechanical and optical characteristics of highly transparent NbO_x thin films deposited with DIBS were systematically studied. E_i and I_i of the secondary ion source weakly affected the optical and the mechanical characteristics of deposited films, while the refractive index was found to slightly decrease with increasing E_i. The most significant effect of the secondary ion beam was on the average compressive stress, which decreased by 50% when the secondary ion beam source was on. When deposited under the optimized secondary ion beam conditions (400 eV and 100 mA), high quality optical films for interference filter, and other applications have been obtained. The corresponding thermo-mechanical properties are CTE = 4.9×10^{-6}°C^{-1}, ν= 0.36, *H* = 5.8 GPa, E_r =117 GPa.

ACKNOWLEDGMENTS

This work was supported by a strategic grant from the Natural Sciences and Engineering Research Council (NSERC) of Canada. The authors would like to thank Prof. S. Goldsmith to for helpful discussions and to Mr. F. Turcot for his technical assistance.

REFERENCES

1. J.P. Masse, H. Szymanowski, O. Zabeida, A. Amassian, J.E. Klemberg-Sapieha, L. Martinu, "Stability and effect of annealing on the optical properties of plasma-deposited Ta_2O_5 and Nb_2O_5 films," *Thin Solid Films*, 515, 1674, 2006.

2. K. Kukli, M. Ritala, M. Leskela, R. Lappalainen, "Niobium oxide thin films grown by atomic layer epitaxy," *Chem. Vap. Deposition*, 4(1), 29, 1998.

3. C.C Lee, J.C. Hsu, D.H. Wong, "Low loss niobium oxide film deposited by ion beam sputter deposition," *Optical and Quantum Electronics*, 32, 327, 2000.

4. C.C. Lee, J.C. Hsu, D.H. Wong, "The characteristics of some metallic oxides prepared in high vacuum by ion beam sputtering," *Applied Surface Science*, 171, 151-156, 2001.

5. S. Venkataraj, R. Drese, Ch. Liesch, O. Kappertz, R. Jayavel, M. Wutting, "Temperature stability of sputtered niobium oxide films," *J. Applied Physics*, 91(8), 4863, 2002.

6. B. Hunsche, M. Vergöhl, H. Neuhauser, F. Klose, B. Szyszka, T. Matthee, "Effect of deposition parameters on optical and mechanical properties of MF and DC sputtered Nb_2O_5 films," *Thin Solid Films*, 392, 184-190, 2001.

7. S.H. Mujawar, A.L. Inamdar, S.B. Patil, P.S. Patil, "Electrochromic properties of spray deposited niobium oxide thin films," *Solid State Ionics*, 177, 3333, 2006.

8. J.J. Cuomo, S.M. Rossnagel H.R. Kaufman, *Handbook of Ion Beam Processing Technology*, Part III, p.170, Noyes Publication Park Ridge New Jersey, 1989.

9. L. Martinu, D. Poitras, "Plasma deposition of optical films and coatings: A review," *J. Vac Science. Technol.*, A18(6), 2619, 2000.

10. G.L. Dwivedi and E.C. Subbaro, "Thermal expansion of monoclinic (Alpha) Nb_2O_5," *J. Am. Ceram. Soc.* 56, 443, 1973.

11. T. Chudoba, N. Schwarzer, F. Richter, "Determination of elastic properties of thin films by indentation measurements with a spherical indenter," *Surface and Coatings Technology*, 127, 9, 2000.

12. G.V. Samsonov, *The Oxide Handbook*, 2nd ed., IFI/Plenum, New York, 1982.

13. J. Thurn, M.P. Hughey, "Evaluation of film biaxial modulus and coefficient of thermal expansion from thermoelastic film stress measurements," *J. Appl. Physics*, 95(12), 7892, 2004

14. S. Venkataraj, R. Drese, O. Kappertz, R. Jayavel, M. Wutting, "Characterization of niobium oxide films prepared by reactive DC magnetron sputtering," *Phys. Stat Sol. (a)*, 188(3), 1047 2001.

15. J.E. Klemberg-Sapieha, J. Oberste-Berghaus, L. Martinu, R. Blacker, I. Stevenson, G. Sadkhin, D. Morton, S. McEldowney, R. Klinger, P.J. Martin, N. Court, S. Dligatch, M. Gross, and R.P. Netterfield, "Mechanical characteristics of optical coatings prepared by various techniques: a comparative study," *Applied Optics*, 43(13), 2670, 2004.

16. C.C. Lee, C.L. Tien, J.C. Hsu, "Internal stress and optical properties of Nb_2O_5 thin films deposited by ion beam sputtering," *Applied Optics*, 41(10), 2043, 2002.

17. C.A. Davis, "A simple model for the formation of compressive stress in thin films by ion bombardment," *Thin Solid Films*, 226, 30, 1993.