Subtle local structural variations in oxygen deficient niobium germanate thin film glasses as revealed by x-ray absorption spectroscopy

M A Sahiner[1], A Nabizadeh[1], D Rivella[1], L Cerqueira[1], J Hachlica[1], R Morea[2], J Gonzalo[2], J C Woicik[3]

[1]Seton Hall University, Physics Department, South Orange, NJ 07079, USA
[2]Laser Processing Group, Instituto de Optica, CSIC, Serrano 121, 28006 Madrid Spain
[3]National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

E-mail: mehmet.sahiner@shu.edu

Abstract. The local electronic and crystal structure of niobium-lead-germanate, Nb_2O_5-PbO-GeO_2 (NPG), glass thin films on silicon substrates were probed by XANES and EXAFS. NPG glasses are promising candidates for applications in nonlinear optical devices because they exhibit interesting optical characteristics such as high nonlinear third order optical susceptibility. In this work NPG glasses were prepared with pulsed laser deposition method with varying oxygen partial pressure to induce thin films with different oxygen stoichiometry. Previously, it was shown that oxygen stoichiometry has a very important effect to produce unusual high optical susceptibility. Detailed EXAFS and XANES analyses in a series of NPG thin films revealed the subtle variations in the local environment around Nb atoms and the Nb oxidation states caused by oxygen deficiencies.

1. Introduction

Multicomponent oxide film glasses containing large fractions of transition and post transition metals such as Nb and Pb are promising candidates for integrated photonic devices due to their excellent optical properties. They possess a broad transparence range ($0.4 < \lambda < 8$ μm), low phonon energies (~ 800 cm-1) and finally, they present large linear refractive indices (≥ 2) and nonlinear optical susceptibilities ($\chi(3)$) if compared to silica glasses.[1,2]

However, the practical use of these materials requires in many cases the production of high optical quality thin film glasses. Different thin film preparation methods have been attempted, such as sol-gel, sputtering or pulsed laser deposition (PLD) [3,4,5]. In particular, PLD allows the synthesis of multicomponent oxide thin films, although a careful choice of the deposition parameters is required to obtain smooth films with good optical quality [6]. Moreover, in the specific case of glasses having large contents of transition and post-transition metal oxides, PLD offers unprecedented possibilities to tailor their optical response. This characteristic is of extraordinary relevance in the case of glasses containing Nb_2O_5, since there exists a strong relationship between the Nb_2O_5 content and the magnitude of their nonlinear optical response [7,8]. This behavior has been related to the formation of three dimensional arrangements of [NbO_6] octahedra, which enhance the hyperpolarizability of the glass.

However, conventional structural analysis techniques such as Raman spectroscopy and X-ray photoelectron spectroscopy did not allow to provide an absolute proof of the reduction of Nb and the modification of its local environment in the glasses that were proposed to be responsible for the strong enhancement of the nonlinear response [10]. In this work, we have performed X-ray absorption spectroscopy analysis (XAS) to obtain an exhaustive picture of the local environment of Nb and its oxidation state in the film glasses. In order to study the effect of oxygen deficiency, a series of thin films has been produced at different oxygen pressures. XAS analysis demonstrates that oxygen deficient films have significant fraction of Nb^{4+} that can be as high as 100% for films deposited in vacuum to decrease to values close to 20% for films grown at 5 Pa.

2. Experimental

Niobium-lead-germanate (NPG) thin film glasses were produced by PLD using an ArF excimer laser (λ=193nm, τ=12ns FWHM). The laser beam was focused on a partially crystallized opal bulk NPG target with a nominal composition of 55 Nb_2O5 - 35 PbO - 10 GeO_2 (mol %), that was prepared using standard melting methods as described elsewhere [4]. The laser energy density at the target surface was in all cases ≈2.5 J cm^{-2}. The vacuum chamber was evacuated to a residual pressure of 1×10^{-4} Pa prior film deposition. Films were grown in a broad O_2 dynamic pressure range (10^{-4} Pa ≤ P_{O2} ≤ 10 Pa) on Si substrates held at room temperature and placed at 3 cm from the target surface. The film thicknesses varied between 100-150nm.

In a previous work [6] we demonstrated that NPG films grown at $P_{O2} \leq 1$ Pa were absorbent. Films deposited in vacuum presented a strong oxygen deficiency (> 50%), while the oxygen content in the films increased with P_{O2} up to a value that was ≈80% that of the bulk target at P_{O2}= 5 Pa. Only films grown above this pressure presented an excess of oxygen, but this worsened their optical response [6]. Thus, NPG films grown at 5 Pa were selected for further optical characterization [9,10].

Details of the optical characterization techniques can be found elsewhere [4,6,9].

In the present work we have performed glancing incidence EXAFS and XANES measurements at the X23A2 beamline of National Synchrotron Light Source at Brookhaven National Laboratory to obtain an exhaustive picture of the local environment of Nb and its oxidation state in the film glasses. The Nb K absorption edge (18986 eV) was used in the EXAFS data acquisition in the fluorescence detection mode with a 0.5º angle of x-ray incidence. Nb metal foil was used for energy calibration. University of Washington's Feffit EXAFS analysis and fitting code was used in for data analyses and EXAFS fittings. The EXAFS functions, χ(k)'s were obtained by subtracting the atomic absorption background using the AUTOBK code [11]. The resultant functions were Fourier Transformed (FT) using a Gaussian window set for 2.0 – 12.0 $Å^{-1}$ k-range. The theoretical EXAFS functions were calculated using University of Washington's FEFF8.4 code [12].

3. Results

In Figure 1 Fourier Transformed (FT) EXAFS data for all the PLD prepared films on silicon substrates at different partial oxygen pressures were shown. Also shown in the figure are the FT data for the NbO_2 and Nb_2O_5 polycrystalline samples for comparison purposes. Vacuum means that there was no oxygen flooding during the deposition of the thin film. The first shell below is dominated by Nb-O scattering paths so the first shell peak is sensitive to oxygen coordination around the Nb atoms. In Figure 1, the first shell peaks below 2 Å for the NPG thin films exhibit an evolution from NbO_2 to Nb_2O_5 structure increasing partial oxygen pressure set during the depositions. Increasing the oxygen partial pressure during the pulsed laser deposition can dramatically decrease the oxygen deficiency and could also induce structural changes in the synthesized thin films. With increasing oxygen pressure, the oxygen deficiency in these thins films diminishes and furthermore the local structure around the Nb atoms is pushed from NbO_2 (tetrahedrally coordinated) to Nb_2O_5 (octahedrally coordinated) symmetry.

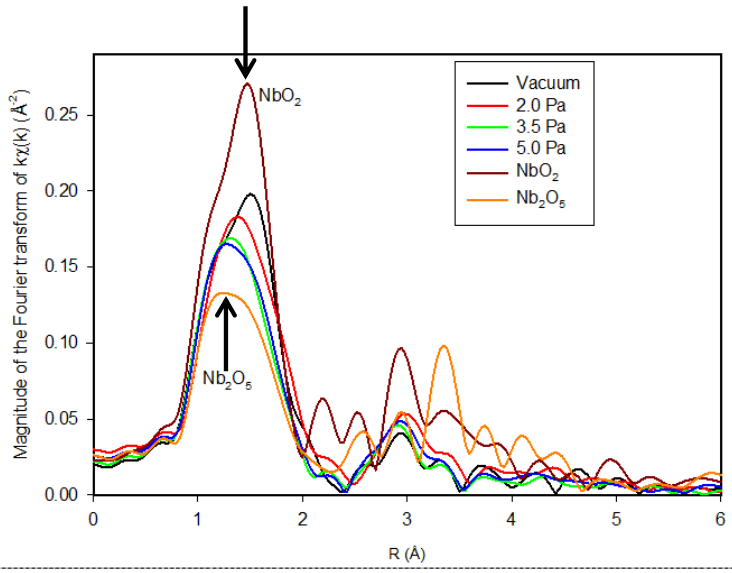

Figure 1. FT EXAFS data for the Nb K edge for Nb_2O_5-PbO-GeO_2 (NPG), glass thin films on silicon substrates NPG thin films with deposited with O_2 varying partial pressure. Also shown in the figure FT EXAFS data for NbO_2 and Nb_2O_5.

In Figure 2, Nb K-edge x-ray absorption near-edge spectroscopy (XANES) results are shown for the vacuum and the 5 Pa sample. NbO_2 and Nb_2O_5 XANES data are also plotted for comparison. NbO_2 does not exhibit a pre-edge peak as well as the vacuum sample whereas, Nb_2O_5 and 5 Pa samples have pre-edge peaks indicating a similar local symmetry. The XANES post-edge features also align well for the NbO_2 and the NPG film deposited with no oxygen flooding (vacuum). Similarly, XANES post-edge features 5 Pa film is in better alignment with Nb_2O_5. Therefore, qualitative XANES analyses support the EXAFS observations that oxygen deficiency pushes the local structure towards NbO_2 crystal symmetry.

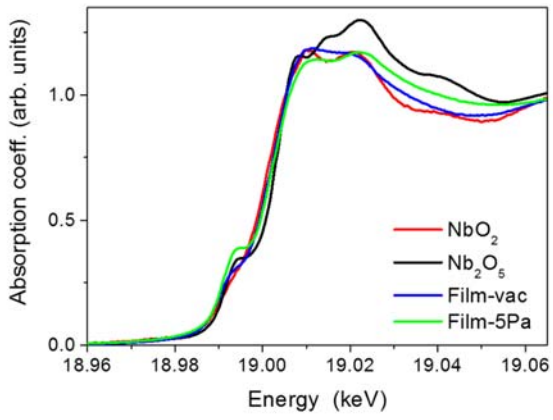

Figure 2. XANES data for the Nb K edge for Nb_2O_5-PbO-GeO_2 (NPG), glass thin films on silicon substrates NPG thin films with deposited under vacuum and with 5 Pa oxygen partial pressure. Also shown in the figure FT EXAFS data for NbO_2 and Nb_2O_5.

In Figure 3, background subtracted χ(k)'s for the NPG thin films and corresponding first-shell EXAFS fits are shown. The EXAFS fits were performed using FEFF8.4 calculated χ(k)'s for NbO_2 and Nb_2O_5 with Nb_2O_5/NbO_2 ratios are floated. Similar analyses to our previous Hf based high-k dielectric thin films in determining the mixed non-equilibrium crystal phases by using weighted EXAFS analyses of the existent structures were used in these thin films.[13-15]. The FT data overlays and EXAFS fits in R-space are shown in Figure 4. The fits were performed on the first-shell since the first-shell peak is well resolved and it is the determining factor in distinguishing the crystal symmetry between NbO_2 versus Nb_2O_5 environment.

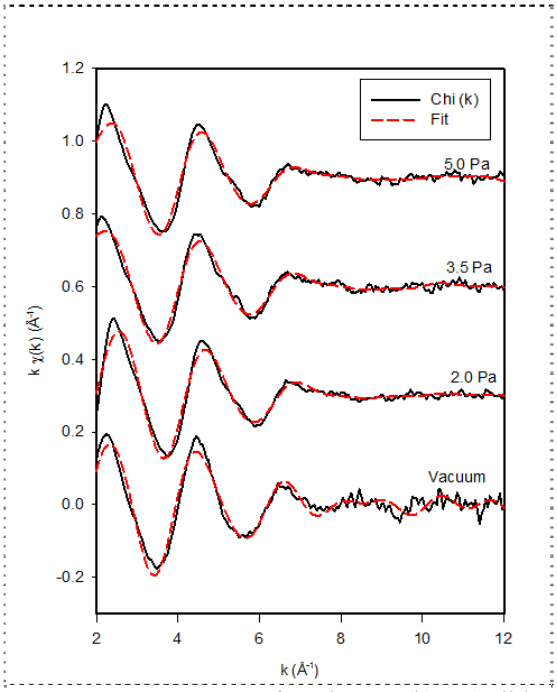

Figure 3. EXAFS functions, χ(k)'s (solid-black lines) and EXAFS fits (dashed-red lines) for the PLD deposited NPG thin films under different partial O_2 pressures.

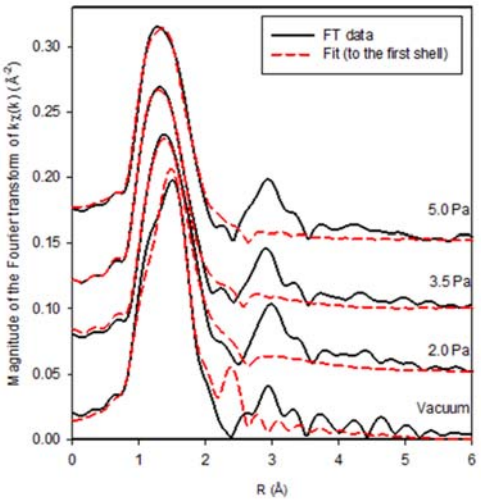

Figure 4. Overlays of the FT EXAFS data (solid-black lines) and EXAFS fits (dashed-red lines) for the PLD deposited NPG thin films under different partial O_2 pressures.

The ratio of the NbO_2 to Nb_2O_5 for all the films are listed in Table I. The vacuum deposited thin film has no Nb_2O_5 contribution and increasing P_{O2} pulls the symmetry towards octahedral Nb_2O_5 structure.

Table 1. The ratio of Nb_2O_5 to NbO_2 content as determined by the weighted EXAFS fits.

Sample	Nb_2O_5/NbO_2 (%)
Vacuum	0.0
2.0 Pa	60 ±3
3.5 Pa	70 ±3
5.0 Pa	80 ±4

The EXAFS fit results for near-neighbor distances, coordination numbers, and Debye-Waller factors for the first-shell are listed in the Table 2. In these fits, the coordination numbers are not varied but used from the crystal symmetry values. The Debye-Waller factors for the first shell are varied but constrained to be equal to each other for all Nb-O near neighbor distances to limit the floating parameters in the fits. The R values are listed in a range in Table 2. The differences in Nb-O near-neighbor distance for NbO_2 and Nb_2O_5 from fit results are noted.

Table 2. The ranges of Nb-O near-neighbor distances, Nb-O coordination numbers, and Debye-Waller factors from to the first-shell EXAFS fits of the NPG thin films.

	First-Shell Fits					
	NbO_2 (I 41/a :1)			Nb_2O_5 (C 1 2 1)		
Sample ID	R(Å) (±0.03)	N_{Nb-O}	σ^2(Å^2)	R(Å) (±0.03)	N_{Nb-O}	σ^2(Å^2)
Vacuum	1.93-2.29	6	0.006±0.001			
2.0 Pa	1.95-2.24	6	0.007±0.001	1.56-1.98	6	0.006±0.001
3.5 Pa	1.95-2.21	6	0.006±0.001	1.53-1.96	6	0.007±0.001
5.0 Pa	1.96-2.21	6	0.008±0.001	1.52-1.96	6	0.008±0.001

4. Conclusion

EXAFS and XANES analyses on the pulsed laser deposited niobium-lead-germanate films showed that the partial oxygen pressure during the deposition was crucial in establishing in the final crystal symmetry around the Nb atoms. EXAFS fits determined the ratio of Nb_2O_5/NbO_2 for the films deposed in various partial oxygen pressures. NPG film deposited with no oxygen flooding exhibits NbO_2 symmetry whereas, for the NPG film deposited at 5 Pa the Nb_2O_5 to NbO_2 ratio is 80%.

References

[1] Lines M E 1991, *J. Appl. Phys*. **69** 6876
[2] Vogel E M, Weber M J and Krol D M 1991 *Phys. Chem. Glasses* **32** 231
[3] Hashimoto T and Yoko T 1995 *Appl. Opt.* **34** 2941
[4] Gonzalo, Sanz O, Perea A, Fernandez-Navarro J M, Afonso C N and Garcia-Lopez J, 2003 *Appl. Phys. A.* **76** 743
[5] Intyushin E B and Novikov V A 2008 *Thin Solid Films* **516** 4194
[6] Sanz O, Gonzalo J, Perea A, Fernandez-Navarro J M, Afonso C N and Garcia-Lopez J 2004 *Appl. Phys. A.* **79** 1907
[7] Flambard A, Videau J, Delevoye J L, Cardinal T, Labrugre C, Rivero C A, Couzi M and Montagne L, 2008 *J. Non Cryst. Sol.* **354** 3540
[8] Royon A, Canioni L, Bousquet B, Rodriguez V, Couzi M, Rivero C, Cardinal T, Fargin E, Richardson M and Richardson K, 2007 *Phys. Rev. B* **75** 104207
[9] Gonzalo J, Fernandez H, Solis J, Munoz-Martin D, Fernandez-Navarro J M, Afonso C N and J. Fierro J L G 2007 *Appl. Phys. Lett.* **90** 251907
[10] Munoz-Martin D, Ruiz de La Cruz A, Fernandez-Navarro J M, Domingo C, Solis J and Gonzalo J 2011 *J. Appl. Phys* **110** 023522
[11] Ankudinov L, Ravel B, Rehr J J and Conradson S D 1998 *Phys. Rev.* B **58** 7565.
[12] Newville M, Livins P, Yacoby Y, Rehr J J, and Stern E A 1993 *Phys. Rev.* B **47** 14126
[13] Lysaght P, Woicik J C, Sahiner M A, Lee B-H, Jammy R 2007 *Appl. Phys. Lett.* **91** 122910
[14] Sahiner M A, Lysaght P S, Woicik J C, Park C S, Huang J, Bersuker G, Taylor W, Kirsch P D and Jammy R 2012 *Phys. Status Solidi* (a) **209** 679
[15] Sahiner M A, Lysaght P S, Price J, Kirsch P D, Woicik J C, Klump A, Reehil C, Manners W A, and Nabizadeh A 2014 *Appl. Phys.* A **117** 93