

Effects of temperature and oxygen pressure on binary oxide growth using aperture-controlled combinatorial pulsed-laser deposition

Nabil D. Bassim^a, Peter K. Schenck^{a,*}, Eugene U. Donev^b, Edwin J. Heilweil^c,
Eric Cockayne^a, Martin L. Green^a, Leonard C. Feldman^b

^a Ceramics Division, National Institute of Standards & Technology, Gaithersburg, MD 20899, United States

^b Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235, United States

^c Optical Technology Division, National Institute of Standards & Technology, Gaithersburg, MD 20899, United States

Received 9 January 2007; accepted 18 May 2007

Available online 17 July 2007

Abstract

In pulsed-laser deposition (PLD), there are many processing parameters that influence film properties such as substrate–target distance, background reactive gas pressure, laser energy, substrate temperature and composition in multi-component systems. By introducing a 12.7-mm diameter circular aperture in front of a 76.2-mm silicon wafer and rotating the substrate while changing conditions during the PLD process, these parameters may be studied in a combinatorial fashion, discretely as a function of processing conditions. We demonstrate the use of the aperture technique to systematically study the effects of oxygen partial pressure on the film stoichiometry and growth rate of VO_x, using Rutherford backscattering spectrometry (RBS). In another example, we discuss the effect of growth temperature on TiO₂ films characterized by X-ray diffraction and Fourier transform far-infrared (Terahertz) absorption spectroscopy. We demonstrate that we have considerable combinatorial control of other processing variables besides composition in our combi-PLD system. These may be used to systematically study film growth and properties.

© 2007 Elsevier B.V. All rights reserved.

PACS : 81.15Fg

Keywords: Combinatorial; Thin films

1. Introduction

Pulsed-laser deposition (PLD) is a film growth technique with many important advantages for the combinatorial growth of oxide thin-film libraries. PLD involves the striking of a target material (in our case a sintered ceramic target) with a series of short laser pulses to cause an explosive ejection of material from the surface of the target in the form of plume, which travels towards a heated substrate for deposition as a film. This deposition is usually performed under high-vacuum conditions, or with a low background pressure of reactive gas. The cation

stoichiometry in the target is generally transferable to the film, and the film deposition apparatus is relatively simple [1].

Despite the simplicity of the film deposition apparatus, there remain some PLD processing parameters that must be addressed in order to optimize film properties and to develop the conditions in processing space for growth of technologically interesting composition libraries. These parameters include the substrate temperature, laser fluence, and background gas pressure. Since these processing parameters are not amenable for study over a continuous range of values, they have to be studied in a discrete, systematic way.

One way to study PLD deposition conditions in a discrete way is to use an artificial mask that allows the deposition of small-area thin films. We designed a simple 12.7-mm diameter mask which we place in close proximity to the substrate and through which we grow discrete films. In our commercial PLD system, we employ 76.2-mm substrates. We can rotate to 12 discrete positions and therefore obtain 12 separate processing

* Corresponding author at: National Institute of Standards & Technology, 100 Bureau Drive, Stop 8520, Gaithersburg, MD 20899-8520, United States.
Tel.: +1 301 975 5758.

E-mail address: pkschenck@nist.gov (P.K. Schenck).

conditions. Fig. 1(a) is a schematic of such a mask and its interaction with the laser plume, and Fig. 1(b) is a photograph taken during ablation showing the effect of the aperture. Fig. 1(c) is a photograph of one such library grown from a TiO₂ target at different processing temperatures.

Using the above configuration, we demonstrate that we can assemble a set of discrete combinatorial libraries that characterize the effect of experimental parameters on film growth and properties. We offer two examples: the first in

which background oxygen pressure was varied during the growth of VO_x, and a second in which substrate temperature was varied during the growth of TiO₂.

2. Experiments and results

The Si wafers were loaded into the PLD chamber through a load lock so as to preserve vacuum. Base pressure of the vacuum system was less than 7×10^{-4} Pa. All samples were grown with a laser energy of 300 mJ, which corresponds to a flux of 15 J/cm² on the target. Prior to deposition, a dummy wafer was inserted and the target was preconditioned as the aperture position was adjusted in order to capture the region with the highest growth rate. The libraries were grown in the following sequence: set highest level of parameter (temperature and oxygen partial pressure), fire laser, rotate substrate, reduce parameter level, fire laser, and so on.

2.1. Oxygen partial pressure variation

For oxygen stoichiometry measurements, we attach small graphite pellets to the surface, which act as substrates for RBS to avoid peak overlap in the measurement of oxygen. The samples that were grown with varying oxygen stoichiometry were grown at room temperature. All libraries were grown from high oxygen pressure to low oxygen pressure in order to avoid annealing effects. The pressures utilized were 13.3, 6.7, 4.0, 2.0, 0.7 Pa and base vacuum. Two VO_x libraries were grown using V₂O₃ and V₂O₅ pressed-powder targets. Vanadium oxide is a material of interest since two variants, V₂O₃ and VO₂, are model Mott-Hubbard materials systems and have semiconductor–metal phase transitions [2–4]. In the case of VO₂, the transition occurs near room temperature, and this holds promise for applications as sensors or switches [5]. The samples were also characterized by X-ray diffraction (XRD).

The stoichiometry and thickness of each VO_x film were determined by RBS. In our setup, a beam of 1.8-MeV helium ions (⁴He⁺), generated by a single-ended Van de Graaff accelerator, impinges upon the sample through a small aperture in a surface-barrier detector (Au–Si), while the backscattered ⁴He⁺ ions are collected by the active area of this annular detector ($\theta \approx 175^\circ$). The resulting voltage pulses are sorted and stored by a multichannel analyzer according to their heights, which are proportional to the energy of backscattered ions.

The number of counts (yield) accumulated in a given channel is directly proportional to the areal density of atoms in a thin layer of the target material, so that the total yield from all the channels spanned by a spectral peak, minus the counts due to background noise, corresponds to the abundance of a given element in the target material. Thus, the stoichiometry of each film was obtained from the ratio of V and O yields, after background subtraction and normalization by the ratio of screened Rutherford scattering cross-sections. The yield from a bismuth (Bi) calibration standard (a shallow implant of 5×10^{15} Bi-atoms/cm² into a Si substrate) was used to obtain absolute values for the V and O areal densities, and hence estimate the thickness of each film. For analytical completeness, an off-the-shelf

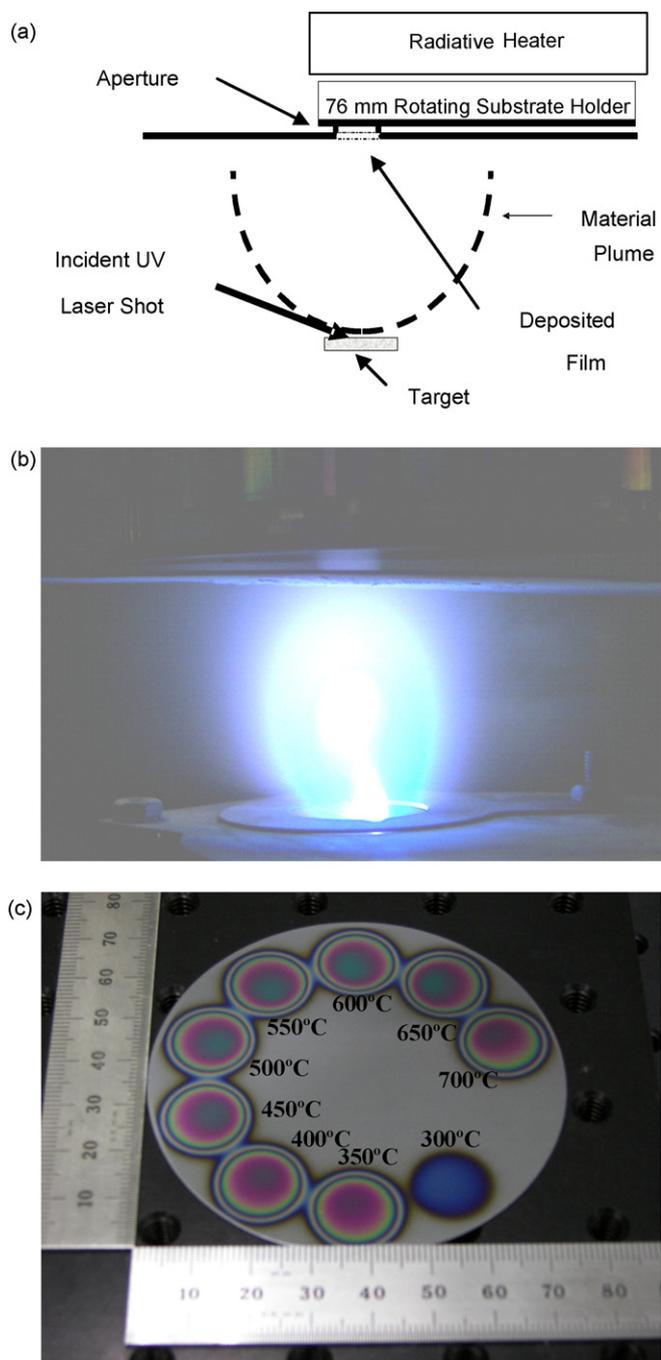


Fig. 1. (a) Engineering schematic of aperture configuration, (b) image of material plume translating through the aperture onto the substrate and (c) photograph of TiO₂ library grown at different processing temperatures, as indicated.

software package was employed to simulate one of the experimental RBS spectra (Fig. 2(a)).

Fig. 2(b) is a photograph of the V_2O_x library grown from the V_2O_3 target and Fig. 2(c) is a plot of the oxygen content in the films as a function of reactive oxygen pressure in the chamber. It is observed that the oxygen pressure in the chamber plays a large role in the total oxygen stoichiometry of the film. It is also apparent that the oxygen incorporation into the film is interface-controlled, i.e., it occurs during the deposition, while diffusion from the atmosphere (after removal from the chamber) does not play a significant role in changing the oxygen stoichiometry.

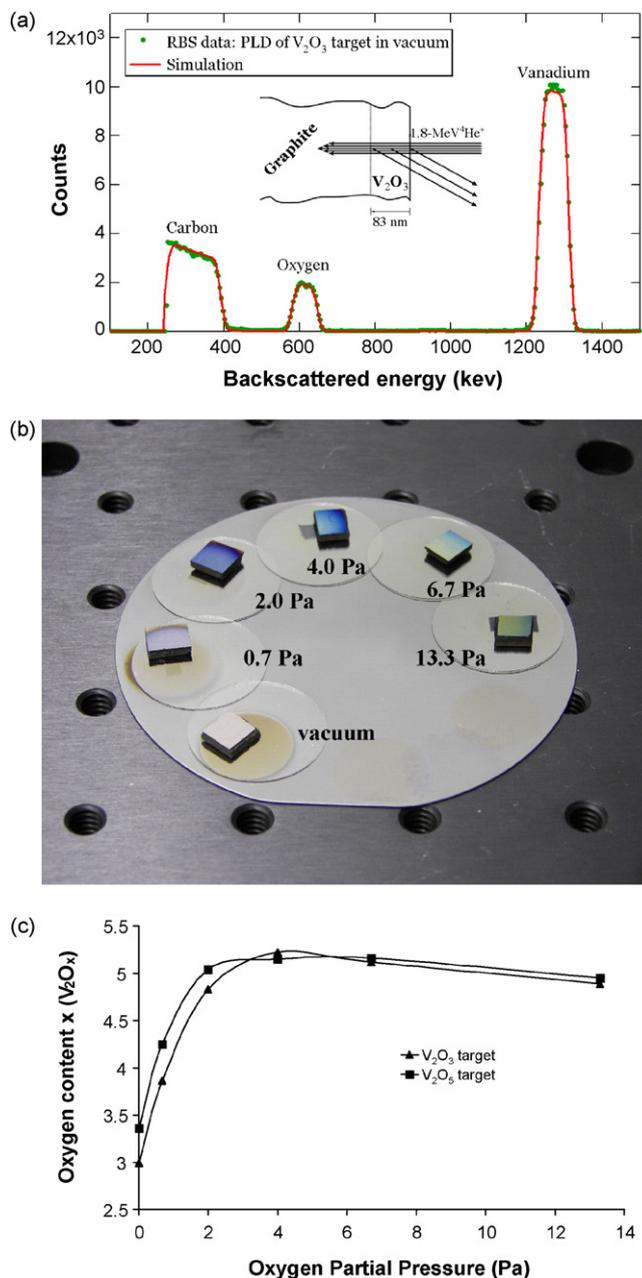


Fig. 2. (a) Experimental and simulated RBS spectra for one of the V_2O_x films (from V_2O_3 target in vacuum): $x = 2.99 \pm 0.02$, thickness = 83 nm; (inset) RBS schematic. (b) Photograph of V_2O_x library with indicated changes in oxygen partial pressure. (c) Oxygen stoichiometry in the library as a function of background pressure of oxygen.

We also demonstrate that, by simply changing the background pressure, a film of average stoichiometry from $x \approx 3$ to 5 may be grown. By XRD, we determined that these films are either amorphous or nanocrystalline. Further studies are underway to anneal and crystallize these films and measure their stoichiometry, in order to determine in more detail the oxygen incorporation mechanism.

2.2. Temperature variation

TiO_2 and mixed-alloys containing TiO_2 are of technological interest for many applications, including high- k dielectrics [6,7] and spintronics [8]. We used a rutile TiO_2 target in order to study the possibility of varying the growth temperature in our aperture libraries. The substrate was heated to 700 °C. Each spot was grown after lowering the temperature by 50 °C from the previous deposition. The films were grown with a 10 mTorr partial pressure of flowing O_2 . After each deposition, the gas valve was closed so as to eliminate a further reaction/annealing of the films in oxygen.

Characterization of the microstructure and chemical bonding states were performed in two ways: Fourier transform far-infrared (Terahertz) absorption spectroscopy and X-ray diffraction. Infrared transmission absorption spectra in the 1.5–21 THz ($50\text{--}700\text{ cm}^{-1}$) range were obtained for each combinatorial spot using a modified Nicolet Magna 550 Fourier transform infrared spectrometer (FTIR) with a Si-coated broadband beam-splitter and DTGS room-temperature detector fitted with a high-density polyethylene window. All measurements were made at room temperature after about 1 h of sample-compartment purging to eliminate water vapor interference and were obtained at 4 cm^{-1} spectral resolution with averaging of 64 interferometric scans. In standard fashion, spectra were converted to optical density (OD) units after ratioing each raw sample transmission spectrum (T_{sample}) to that from an unexposed region of the same Si disk (T_{blank}), i.e., $OD = -\log_{10}(T_{\text{sample}}/T_{\text{blank}})$, obtained under identical acquisition conditions. XRD was also performed for each spot using a standard $\theta\text{--}2\theta$ geometry.

Fig. 3(a) is an XRD scan showing that the dominant phase at high processing temperatures is the rutile phase, and that at low temperatures the anatase phase is also present in a two-phase mixture from 350 to 400 °C. At 300 °C, the film appears to be nanocrystalline or amorphous. It is apparent that the texture of the films also varies as a function of temperature, with a (1 1 0) texture in the rutile phase at middle temperatures (450–550 °C) with a strong peak at $2\theta \approx 27^\circ$, and a (2 0 0) texture at higher temperatures with $2\theta \approx 39^\circ$ becoming much more intense relative to a powder diffraction prediction.

Terahertz spectroscopy is extremely sensitive to local environmental interactions and crystalline structure of solid-state samples [9]. As with X-ray analysis, small changes in crystal lattice constants and molecular orientation appear in the phonon absorption structure in this spectral region. Fig. 3(b) clearly shows two types of spectral components from crystalline phases (narrowband features) that change in intensity and composition as a function of deposition

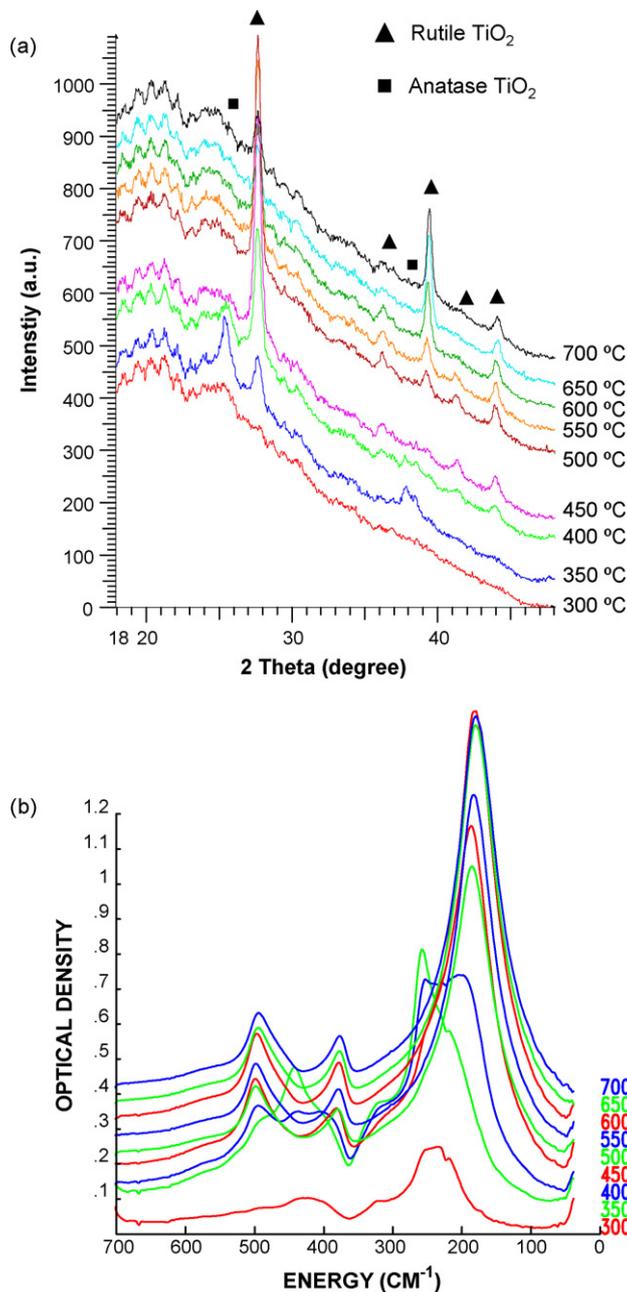


Fig. 3. Results of TiO_2 combinatorial library showing change in phase formed as a function of temperature: (a) XRD spectra showing that the rutile phase forms at higher temperatures, with a two-phase region, which includes the anatase phase, at 350–400 °C and (b) Terahertz absorption spectra showing a change in dominant absorption peaks from higher deposition temperatures to lower temperatures corresponding to a high temperature rutile and medium temperature anatase phases. Each spectrum is offset by OD = 0.05 for ease in reading.

temperature. First-principles density functional theory (DFT) calculations were used to corroborate the identity of the observed phases. Given a crystalline structure, it is possible to

use DFT calculations to calculate its phonon frequencies. Previous works have reported calculated phonon frequencies for TiO_2 in its rutile [10] and anatase [11] phases. We have recalculated the frequencies of the two phases using the VASP code [12] with projected augmented wave pseudopotentials [13]. Calculation details are described in Cockayne and Burton [14]. For the rutile phase, infrared-active peaks are calculated at 82, 120, 367, and 471 cm^{-1} , while for the anatase phase, infrared-active peaks are calculated at 239, 347, and 422 cm^{-1} . Fig. 3(b) is consistent with a high-temperature rutile phase and an intermediate-temperature anatase phase. All predicted phonons are seen (with the exception of the two lowest frequency phonons in the rutile phase which are assumed to overlap). Further work is being performed in order to establish the exact transition point and to determine whether single-phase anatase can be obtained using our PLD process.

3. Conclusions

We have demonstrated a simple aperture technique which allows us to effectively create discrete combinatorial libraries that are useful for exploring the parameter space related to film growth. We have shown that (1) oxygen content in a PLD-grown film is strongly dependent on the background gas pressure, and that (2) we can systematically vary the temperature in a library to observe microstructural effects using the aperture technique.

References

- [1] Pulsed Laser Deposition of Thin Films, vol. 1, John Wiley & Sons, New York, 1994.
- [2] C. Castellani, C.R. Natoli, J. Ranninger, Phys. Rev. B 18 (1978) 5001.
- [3] C. Blaauw, F. Leenhouts, F. Vanderwoude, G.A. Sawatzky, J. Phys. C-Solid State Phys. 8 (1975) 459.
- [4] G.A. Thomas, D.H. Rapkine, S.A. Carter, A.J. Millis, T.F. Rosenbaum, P. Metcalf, J.M. Honig, Phys. Rev. Lett. 73 (1994) 1529.
- [5] J.Y. Suh, R. Lopez, L.C. Feldman, R.F. Haglund, J. Appl. Phys. 96 (2004) 1209.
- [6] G.D. Wilk, R.M. Wallace, J.M. Anthony, J. Appl. Phys. 89 (2001) 5243.
- [7] O. Auciello, W. Fan, B. Kabius, S. Saha, J.A. Carlisle, R.P.H. Chang, C. Lopez, E.A. Irene, R.A. Baragiola, Appl. Phys. Lett. 86 (2005).
- [8] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, H. Koinuma, Science 291 (2001) 854.
- [9] M.R. Kutteruf, C.M. Brown, L.K. Iwaki, M.B. Campbell, T.M. Korter, E.J. Heilweil, Chem. Phys. Lett. 375 (2003) 337.
- [10] P. Ghosez, E. Cockayne, U.V. Waghmare, K.M. Rabe, Phys. Rev. B 60 (1999) 836.
- [11] M. Mikami, S. Nakamura, O. Kitao, H. Arakawa, Phys. Rev. B 66 (2002).
- [12] G. Kresse, J. Furthmuller, Phys. Rev. B 54 (1996) 11169.
- [13] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
- [14] E. Cockayne, B.P. Burton, Phys. Rev. B 62 (2000) 3735.