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Metal/metal-oxide/metal etalon structures grown by pulsed laser deposition

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ABSTRACT Multilayered metal/metal-oxide/metal structures are fabricated by pulsed laser deposition in alternating non-reactive and reactive oxidising conditions, by using pure metal targets. The variety of metals used includes tantalum, zinc and indium. Further to the well-known interferometric, etalon, optical behaviour the structures feature additional activation properties owing to the nanoscopic nature of the oxide materials incorporated.

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1 Introduction

Pulsed laser deposition (PLD) exhibits several unique features that can be employed advantageously in the growth of materials for photonics applications. Significant recent examples include, first, the high optical quality, complex crystalline structures required for the successful realization of waveguide laser sources [1]. The multi-component plasma produced by high intensity ultraviolet laser pulses enables the epitaxial growth of, the otherwise hard-to-grow, materials such as Ti-Sapphire and Nd : GGG at quite high growth temperatures. Second, the innovative nanoscopic metal oxides grown at room temperature are exhibiting unique properties [2]. Owing to their nature, they feature a range of fundamental optical and electronic interactions that may lead to holographic storage and sensing applications. These functional properties may be suitably tuned by controlling the materials structure in the nanoscale regime [3] via the particular growth conditions. In effect, not only the growth but also the ambient operational conditions influence their functionality [4].

A wide range of oxide materials has been grown so far by reactive and non-reactive PLD using respectively metal or oxide targets. Various attempts towards simple multilayered structures have been made. Targeting to enhance the conductometric sensing properties, alternating indium and tin oxides have been reported [5] with encouraging results. Furthermore, heterogenous multilayers have been presented using alternating targets in laser ablation experiments [6] in which copper nanoparticles are incorporated in alumina matrix.

In this work we report, for the first time to our knowledge, on the growth of metal/metal-oxide/metal ($M/MO_x/M$) multilayers in the form of lossy Fabry-Perot etalon structures. Materials are grown in single PLD runs at room temperature by using pure metal targets, such as tantalum, zinc and indium, in an alternating reactive/non-reactive mode, by externally controlling the growth atmosphere. Various experiments have been carried out by utilizing KrF (248 nm), ArF (193 nm) or Nd : YAG (532 nm and 355 nm) nanosecond laser pulses. The integrated structures grown exhibit excellent optical quality and incorporate oxides of an active nanoscopic nature. First growth results, optical properties and functional performances of exemplar structures are presented.

2 Experimental techniques

A multi-port stainless steel reactor equipped with gas control facilities was used for the present PLD experiments. Nanosecond laser sources used include an excimer laser operating as ArF at $\lambda = 193$ nm or KrF at $\lambda = 248$ nm. Alternatively, a Nd : YAG at $\lambda = 532$ nm and 355 nm were also used. All lasers were operating at a 10 Hz repetition rate. Single beam and dual beam experiments have been performed.

The metal targets (including Ta, Zn, In) of 99.998% purity were attached on a two-axis motor driven translating holder. The laser beam used for ablation was focused on the target. Maximum energy density values are ranging typically as for KrF: 5.0–6.0 J/cm^2, ArF: 2.0–3.0 J/cm^2, Nd(2ω): $\sim 20.0\ J/cm^2$, Nd(3ω): $\sim 10.0\ J/cm^2$. An angle of incidence of 45° to the target was nominally used. The glass receiving substrate, also fixed on a moving holder, was positioned at ∼4 cm distance from the target.

Series of preliminary experiments have been carried out for investigating the growth of single metal and single oxide thin films and establishing the appropriate growth conditions for achieving optical quality materials. High vacuum at pressure of 2×10^{-3} Pa was used for pure metal growth. The reactive oxygen pressure for oxide growth was varied from 10 to 60 Pa. For the present experimental conditions, below the lower end of the above range films grown were turning to

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become metallic, while above the upper end films were becoming porous.

Trilayer and multilayer optical etalon structures were grown on glass substrates at room temperature in single experimental runs by alternating between oxygen reactive and non-reactive atmosphere conditions. The background pressure of the reactor was 2×10^{-3} Pa and all non-reactive PLD growths performed at this pressure resulted in pure metallic films. For the reactively grown oxide layers, the molecular oxygen pressure was kept in the range of ∼15.0 Pa, found to produce best structural properties in the present context. Experiments were performed under static pressure conditions and the reactor was fully evacuated to the background pressure for the non-reactive mode.

All films grown exhibit excellent adherence and smoothness. The produced structures have been studied for their interferometric performance by use of a Perkin Elmer-Lambda 9 Spectrophotometer in the range of 300–1600 nm. The variation of their optical transmission, reflection and absorption with wavelength was recorded. Structures remaining in ambient atmosphere for several months show a nearly identical behaviour. Even though, in some cases, some oxidisation effects of the outer metallic layer are apparent, which slightly modify the spectral performance.

The functional behavior of the interferometric structures under temperature variation has been studied in single wavelength experiments. A schematic of the experimental setup for recording the optical behaviour of the structures with temperature is depicted in Fig. 1. The etalon is placed inside an especially made cylindrical low-temperature (to 200 °C) oven, externally controlled by a thermo-controller device. The p-polarized beam emitted by a He : Ne laser (5 mW power at $\lambda = 633$ nm) is used. Part of the incident beam is used for calibration purposes. The structure is positioned at the Brewster angle, in respect to the glass substrate, in order to avoid interference effects that may become detrimental in case of thermal expansion or deformation of the substrate. Tests were performed by using plain and single-layer coated substrates to verify the absence of such systematic thermal effects. The full temporal evolution of the output signals was recorded by means of calibrated amplified photodiodes and a computer controlled data acquisition system. Respective values at stabilized temperature conditions were also recorded.

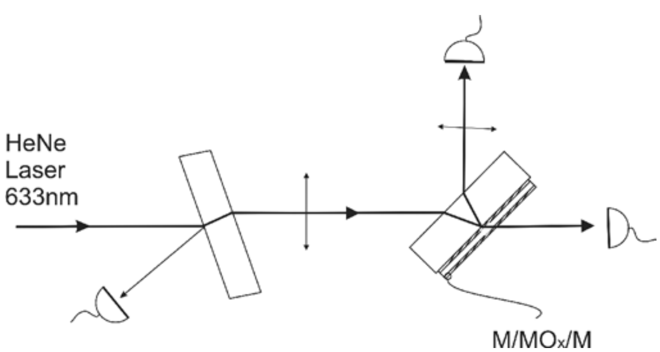

FIGURE 1 Schematic of the experimental configuration used for studying etalon performance as a function of temperature.

3 Results and discussion

The growth parameters control the thickness and the nature of each layer and reflect on the size, the position and shape of interference fringes. Several structures have been obtained by varying deposition time, laser wavelength and fluence for each growth run. PLD is thus proved to be an extremely versatile method for growing multilayered structures.

Oxide layers grown at 1064 nm, appear to be rather opaque and of brownish colouring, in comparison to those grown using UV laser sources at similar conditions. The latter oxides are fully transparent or of a slightly yellow coloration depending on the growth atmosphere. In all cases the absorption edge positioned in the near ultraviolet region (TaO_x: $E_g \sim 3.9$ eV, ZnO_x: $E_g \sim 3.26$ eV, InO_x: $E_g \sim 3.0$ eV) is blurred, indicating the non-crystalline structure of the oxides. However, the use of ultraviolet wavelengths improves the stoichiometry and materials quality due to the dominant photolytic ablation [7, 8], though oxygen pressure remains the most important controlling parameter. In terms of optical quality, films grown at short wavelengths exhibit minimal concentration of particulates and droplets at the surface.

The growth rate for the various materials has been studied in a related series of experiments. For the present experimental conditions values were found in the range of 0.02 to 0.06 Å per pulse. Measurements of the layer thickness were made by using mechanical profilometer instruments (Alphastep 100 and 500-IQ). The thickness of oxide single layers grown under identical conditions was also investigated by optical methods [9]. The total thickness of the grown structures was in the range of 100 nm to 300 nm.

The interferometric response of an exemplar tri-layer $Zn/ZnO_x/Zn$ etalon structure grown on glass is shown in Fig. 2. The thickness of the metal layers affects crucially the overall performance due to the significant values of their complex refractive index. In this particular case the structure was heat-treated as discussed below and its response is found by design to be equivalent to a system of $Zn/ZnO_x/Zn$: 3 nm/250nm/5nm, for which an appreciable reflectivity slope for the He-Ne red laser line exists (Fig. 2). The oxide layers

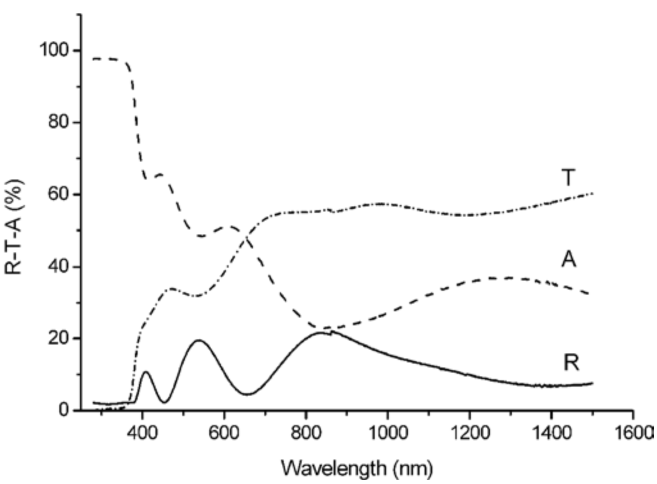

FIGURE 2 Optical transmittance T, reflectance R, and (deduced) absorbance A, for a $Zn/ZnO_x/Zn$ etalon structure grown using 532 nm ns laser pulses. Response after thermal cycling experiments.

grown are seen to be non-stoichiometric under these growth conditions. They are featuring, however, the already discussed nanoscopic structure, comprising nanoparticles (both metal and oxide) embedded in the amorphous oxide background. The presence of such crystalline particles has been verified by TEM studies.

The behaviour of such trilayer structures grown at various conditions has been studied as a function of temperature. The functionality of each particular structure naturally depends on the optical design of the multilayer, however, the variable response observed here is typical for this class of structures.

Fig. 3 depicts the variation of the reflected He : Ne laser beam intensity during a 60 min heating–cooling cycle for the above-discussed zinc-based structure, featuring the macroscopic optical properties presented in Fig. 2. Taking into account the thermal expansion coefficients of the materials in the 250 nm thick structure, it is clear that such an expansion contribution to the observed etalon structure is in the sub-nanometer range (for $\Delta T \sim 100\,^{\circ}C$) and is thus negligible.

The growth parameters and especially the laser wavelength and the oxygen pressure have a crucial influence on the structure and consequently on the optical response. For the particular Zn-based structure grown at 532 nm, a quite strong decrease of the reflected signal (∼50%) with increasing temperature is seen which is reversible for the larger, upper, part of the temperature range. A hysteresis effect is also observed here during the cooling down period.

The observed behaviour is clearly attributed to considerable variations of the complex refractive index in the material caused by its nanoscopic structure. Even though the overall macroscopic functionality depends on the optical design of the structure, the variational response is characteristic of the oxide materials structure and thus depend on the growth conditions. We note here that we have observed minimal such effects in materials grown at short UV (193 nm) wavelengths. By assuming that variations are only due to the real part of the oxide refractive index, a simulation of etalon response shows that such changes tend to approach the extreme figure of 10% of the background refractive index ($n \sim 1.97$). Even though electrons are expected to be thermally excited from localised states to the conduction band, it seems unlikely that the effects are caused solely by free carrier concentration variations (Drude). Oxidisation, charge transfer and local lattice modification are expected to contribute significantly, while the metal interfaces are also expected to play an important role. In effect, such a structure would be best considered as a composite medium, not only in terms of its passive optical behaviour, but also in terms of its optoelectronics functionality. Further research is underway aiming to the understanding of the observed behaviour.

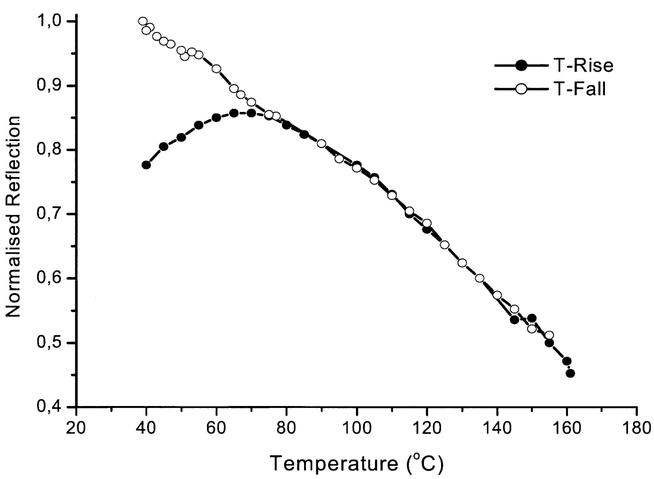

FIGURE 3 Temperature variation of the He-Ne beam intensity reflected off the $Zn/ZnO_x/Zn$ structure of Fig. 2. Response is recorded for increasing and decreasing temperature and the hysteresis effect is noted.

4 Conclusion

Metal/metal oxide/metal optical etalon structures have been grown at room temperature in single PLD runs by controlling the oxygen reactive atmosphere. The optical quality of the grown structures is excellent and systems have been studied for their passive interferometric response. The core oxide part of the structures is non-stoichiometric and exhibit a mixed nanoscopic structure, with crystallites embedded in the amorphous matrix. The structures exhibit a strong temperature dependent optical response, which is seen to be a function of the materials growth conditions. Zn-based structures grown by 532 nm laser pulses demonstrated the largest (50%) decrease of the reflected intensity at 633 nm with increasing temperature, attributed to significant changes of the refractive index of the composite structure. Such activation effects are clearly of further interest and PLD offers the tools for investigating and exploiting these phenomena in photonics applications.

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