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Studies of aluminum oxide thin films deposited by laser ablation technique

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ABSTRACT

This paper presents the structural and optical investigations of the aluminum oxide nanocrystalline thin films. Investigated films were fabricated by laser ablation technique in high vacuum onto quartz substrates. The films were deposited at two different temperatures of the substrates equal to room temperature and 900 K. X-ray Diffraction spectra proved nanocrystalline character and the corundum phase of the film regardless on the substrate temperature during the deposition process. Values of the refractive indices, extinction and absorption coefficients were calculated by using Transmission and Reflection Spectroscopy in the UV–VIS–NIR range of the wavelength. Coupling Prism Method was used for films thickness estimations. Experimental measurements and theoretical calculations of the Third Harmonic Generation were also reported. Obtained results show that the lattice strain may affect obtained values of the third order nonlinear optical susceptibility.

1. Introduction

Aluminum oxide (Alumina, Al_2O_3) or sapphire is one of the most important ceramic materials with exceptional properties such as great hardness, abrasion resistance, mechanical strength, corrosion resistance, good electrical insulation, high melting temperature, fine particle size, large surface area, catalytic surface activity and useful optical properties when compared with other ceramics materials [1–3]. It has many industrial applications including microelectronics, coatings, catalysis, composite materials and advanced material technologies [4–6].

One of the naturally occurring forms of the aluminum oxide known as corundum (α-Al_2O_3) was described the first time in 1798 by Grevill [7]. Although other minerals of this compound such as bauxite (hydroxide mixture of aluminum oxide and water) were previously known. There are many forms of Al_2O_3 crystalline structure including: α, χ, η, δ, κ, θ, γ and ρ phases. An example of α-phase of Alumina is corundum/sapphire. The other forms are frequently termed transition of the Alumina and arise during the thermal decomposition of aluminum trihydroxides under different conditions. The aluminum hydroxides can exist in four well defined forms: the monohydrate AlOOH, as boehmite (γ-monohydrate) and diaspore (α-monohydrate) and the trihydrate $Al(OH)_3$, as gibbsite (γ-trihydrate) and bayerite (α-trihydrate). At high temperatures, all of the heat treatment paths will terminate in α-Al_2O_3 crystalline structure. The paths of transition Al_2O_3 during the heating processes are shown in Fig. 1 [8]. α-phase of Al_2O_3 is the most stable form formed between aluminum and oxygen, and is also the final product of the thermal or dehydroxylation treatments of all the hydroxides. The metastable alumina can be divided into two major groups, depending on the stacking of their O anions: face-centered cubic (fcc) packing (γ, θ, η and δ) and hexagonal close packing (hcp) (κ and χ) [9].

The commonly-used aluminum oxide is produced through the Bayer process starting from crushed bauxite and caustic aluminate solution containing soda. The dissolution reaction is generally carried out under high pressure at temperatures ranging from 150 to 280 °C. The caustic solution reacts with the aluminum hydroxide and the impurities can be separated by sedimentation and filtration, leaving a clear solution. Aluminum oxide's powders can be obtained through heat treatment at their transition temperatures. α-phase of Al_2O_3 produced by the Bayer method have maximum purity of 99.6–99.9%. The demand of the high purity Al_2O_3 α-phase, important for electronic devices such as YAG (Yttrium-Aluminum-Garnet) and Titanium Sapphire laser devices, is still increasing. High purity α-Al_2O_3 is indispensable for manufacturing substrate of the SOS (Silicon on Sapphire) devices being the substrate for epitaxial growth of Si layer, bioceramics, gas sensing or

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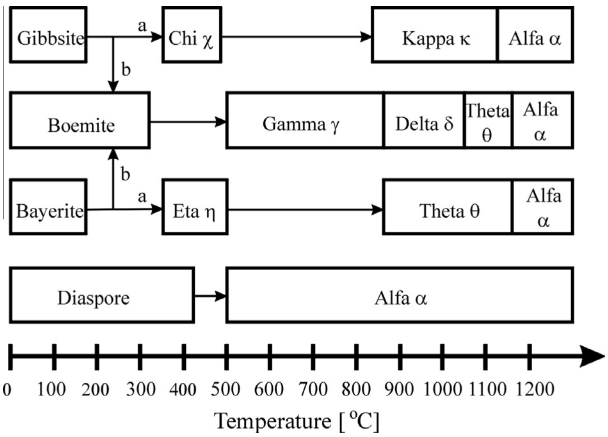

Fig. 1. Structure transformation of aluminum hydroxides and aluminum oxides [11].

catalyst supports. High purity α-phase of Al_2O_3 is also used for applications as optical materials [10].

Many techniques have been used to fabricate different crystal phase of Al_2O_3 thin films, including plasma enhanced chemical vapor deposition (CVD), sol-gel methods and pulsed laser deposition (PLD), etc. [12–17]. CVD techniques for the films consist of the decom position of inorganic or metalorganic precursor in the vapor phase [12–14]. This process can be carried out with or without oxygen at relatively low temperatures and at reduced pressure. Sol-gel method also consists of the inorganic or metalorganic compounds and the process can be carried out at room temperature and atmospheric pressure [15,16]. During the processing of ceramic thin films, the irregular particle sizes and shapes often lead to non-uniform packing morphologies that result in packing density variations. Therefore, for both of these methods uncontrolled flocculation of the inorganic or metalorganic compounds due to attractive van der Waals forces can also give rise to microstructural inhomogeneities of the films. In comparison to these methods, PLD process has some evident advantages, i.e.: possibility of the film's growing at atomic rate [12,17]. The low growth rate of the PLD films is very convenient to prepare nanometer size thin films and super-lattice materials because the growth process can be controlled precisely. In presented experiment, α-phase of Al_2O_3 thin films were fabricated by PLD at two substrate temperatures and the same intensity of the laser beam. We investigated the dependence of structural and optical properties as a function of the growth temperature. This paper presents characterization of the thin films structure investigated by X-ray Diffraction (XRD) technique, studies of the linear optical properties by using classical transmittance spectroscopy and coupled prism method as well as investigations of the nonlinear optical properties by using Third Harmonic Generation (THG) technique.

2. Experiment

Pulsed Laser Deposition is a process during which a pulsed laser beam is used for ablation of the solid target. During this process plasma, which consists of electrons, ions, atoms and excite species, is produced. Although the fractional ionization of the nascent plasma from metal oxides is relatively low, ions can play an important role of the thin films deposition process. Time-of-flight (TOF) mass spectrometry is one of the best methods for the plasma investigation. The resolution of the time-of-flight spectrometer depends on the several parameters, i.e. repeller voltage and repeller pulse time-shape. In our study the repeller voltage system was used for the time-resolved analysis of the plasma plume and degree of the particles ionization [18–20].

Time distribution of the ablated species inside the plasma plume is very important for understanding the PLD processes and also the thin films deposition. The experimental apparatus is shown in Fig. 2. A target of Al_2O_3 was prepared by cold pressing high purity powder (99.999%, Sigma-Aldrich Chemical Company) in air condition. A XeCl excimer laser beam ($\lambda = 308$ nm, $\tau = 20$ ns, repetition: 10 Hz, intensity: 2 J/cm^2) was used for the ablation process. A pulsed field for time-of-flight mass spectrometer was used to investigate the expansion dynamics of the ionic species ejected during laser ablation [21–24]. The ionic plume was produced by irradiation of the powdered Al_2O_3 target by the focused laser beam inside the vacuum chamber. Fig. 3a presents a typical plasma plume of Al_2O_3 during the PLD process. The laser beam was focused on the target and an incident angle between the beam and a surface of the target was equal to 45° (see Fig. 2). The pressure of the vacuum chamber was kept at about 1×10^{-6} mbar. The ablated material was then deposited on the quartz substrate kept at 4 cm from the target and its temperature was equal to: RT (room temperature) and 900 K. Ions and electrons were produced inside an interaction region near the target. The COMSTOCK, model TOF 101 mass spectrometer allowed us to distinguish the positive ions. The positive ions of aluminum oxide were detected shot-to-shot by the tandem multichannel plate (MCP) detector. The signal consisting of the pulses sequence was amplified, introduced to an input of the real time multichannel scaler (RTMS) [25–27] and finally registered by a computer. The computer was also used to control laser's power after each laser pulse. Fig. 3b present a time of flight spectra for aluminum oxide's positive ions captured during 1000 laser shots.

The TOF distributions of the ablated species are well described by Knudsen's theory of thin films formation near the ablation surface. The TOF distribution $n(t)$ is described by a shifted Maxwell-Boltzmann distribution:

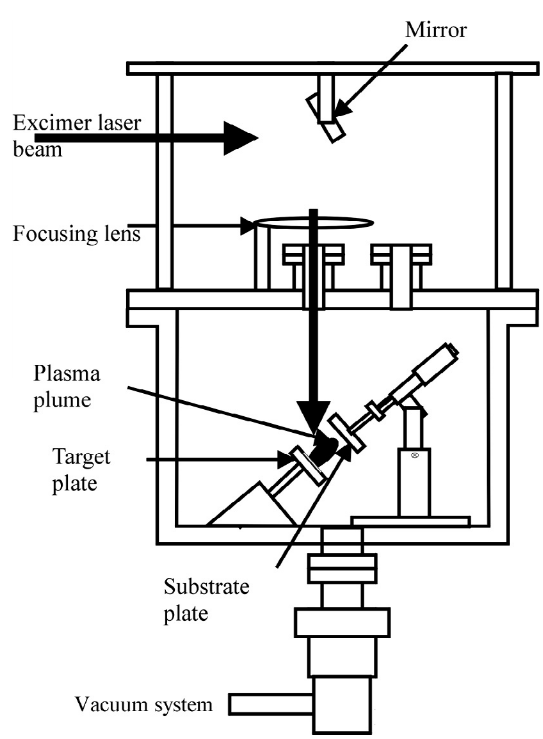

Fig. 2. Experimental setup of the PLD process.