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Optical and structural characterization of pulsed laser deposited ruby thin films for temperature sensing application

Satchi Kumari, Alika Khare*

Laser and Photonics Lab, Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, India

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ABSTRACT

The ruby thin films were deposited by pulsed laser deposition (PLD) technique in an atmosphere of oxygen using ruby pellet, indigenously prepared by mixing Al_2O_3 and Cr_2O_3 in appropriate proportion. The characteristics R_1 and R_2 lines at 694.2 nm and 692.7 nm in the photoluminescence spectra of target pellet as well as that of PLD thin films, confirmed the ruby phase in both. The XRD and Raman spectra confirmed deposition of *c*-axis oriented crystalline ruby thin film on sapphire substrate. Effect of deposition time, substrate and deposition temperature on PLD grown thin films of ruby are reported. The intensity of R_1 and R_2 lines of PLD ruby thin films increased enormously after annealing the film at 1000 °C for 2 h. The film deposited on sapphire substrate for 2 h was 260 nm thick and the corresponding deposition rate was 2.16 nm/min. This film was subjected to temperature dependent photoluminescence studies. The peak positions of R_1 and R_2 lines and corresponding line width of PLD ruby thin film were observed to be blue shifted with decrease in temperature. R_1 line position sensitivity, $d\bar{\nu}/dT$, cm^{-1}/K in the range 138–368 K was very well fitted to linear fit and hence can be used as temperature sensor in this range.

1. Introduction

Ruby is a well known lasing material for high power Q-switched solid-state laser. It consists of sapphire (Al_2O_3) in which a small percentage of Al^{3+} ions has been replaced by Cr^{3+} ions. The Cr^{3+} ion has three d electron in its unfilled shell. Transition among the levels of Cr^{3+} ion gives photoluminescence in visible region of the electromagnetic spectrum. The characteristic photoluminescence occurs at 694.2 nm and 692.8 nm respectively called R_1 and R_2 lines [1]. Ruby possesses favorable combination of relatively narrow line width, a long fluorescent lifetime, high quantum efficiency, and broad and well-located pump absorption bands. In ruby, avalanches of phonons take place by stimulated emission within the Zeeman-split ^2E levels [2,3]. Hence it is shown to behave as a SASER (sound amplification by stimulated emission of radiation) [4]. Nonlinear optical phenomena such as non degenerate two-wave mixing, spectral hole and slow and fast light are reported in ruby crystal [5–8]. Single crystal of ruby is shown to act as fiber optic thermometer [9,10]. It has also been used as an ion-irradiation damage sensor [11]. Ruby thin films have been used to probe the local density of states in complicated photonic systems [12]. The *R* lines of ruby are accompanied by nearby red shifted weak bands in both emission and absorption spectra. These bands are referred as vibronic side bands. These vibronics side bands are predominantly one-phonon transition. This fact makes ruby well suited for phonon-spectroscopy by optical means, which can be used as a detector or tunable generator for high frequency phonons [13–15]. The dependence of R_1 and R_2 line intensity, wavelength and the corresponding fluorescence lifetime as a function of the temperature and pressure makes ruby as the basis for a variety of sensors [16–20]. In order to exploit these properties of ruby in the form of miniaturized sensor for photonics and electro-optic applications, it is required to be grown in the form of thin film. Very high quality epitaxial ruby thin films, free from strain and stress, are highly desirable for these applications.

Ruby thin films were grown via solid phase epitaxy [21], electron beam evaporation [22] and chemical vapor deposition [23]. The deposition of polycrystalline ruby thin film on silicon substrate is reported via pulsed laser deposition (PLD) technique [24]. In the present paper, the effect of deposition time, substrate (quartz and sapphire), substrate temperature and post-annealing on the quality of PLD deposited ruby thin films have been studied. Further its application as temperature sensor in the range 138–473 K is demonstrated through photoluminescence studies.

2. Experimental details

The ruby pellets were prepared by mixing 0.05 wt%, 0.5 wt% and 1 wt% of Cr_2O_3 by weight in γ phase Al_2O_3 powder. The mixed powder was annealed in the furnace for 6 h at 1000 °C to make

* Corresponding author. Tel.: +91 361 2582705; fax: +91 361 2582749.
E-mail address: alika@iitg.ernet.in (A. Khare).

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Table 1
List of PLD deposited ruby samples under various deposition conditions.

Sample name	Deposition parameters				Thickness (nm)	Deposition rate (nm/min)
	Substrate	Deposition time	Substrate temperature	Post-annealing		
Sample 1	Quartz	2 h	RT	–	190	1.5
Sample 2	Quartz	4 h	RT	–	400	1.5
Sample 3 (annealed sample2)	Quartz	4 h	RT	1000 °C for 2 h	400	1.5
Sample 4	Quartz	1 h	650 °C	–	100	1.6
Sample 5	Sapphire	30 min	650 °C	–	55	1.8
Sample 6	Sapphire	1 h	650 °C	–	120	2.0
Sample 7	Sapphire	2 h	650 °C	–	260	2.16
Sample 8 (annealed sample 5)	Sapphire	30 min	650 °C	1000 °C for 2 h	55	1.8
Sample 9 (annealed sample 6)	Sapphire	1 h	650 °C	1000 °C for 2 h	120	2.0
Sample 10 (annealed sample 7)	Sapphire	2 h	650 °C	1000 °C for 2 h	260	2.16

it moisture free. Pellets of diameter 13 mm were prepared from the annealed powder and were sintered for 24 h at 1400 °C and then at 1700 °C for 2 h. Long sintering time results in better diffusion of Cr ions in alumina sites replacing the Al^{3+} ions by Cr^{3+} ions. Small quantity of the pellet (0.5 wt% doped) in the form of powder was subjected to HRTEM studies for confirmation of the ruby phase. The emission and excitation spectra of all the three pellets were recorded by Edinburg instrument, FS-920P (commercial fluorimeter with double monochromator) by exciting with 532 nm light from a Xenon lamp. Confocal image of target pellet (0.5 wt%), was recorded by confocal laser scanning microscope (Carl Zeiss LSM 510 Meta) using 543 nm laser as the excitation source. The experimental set-up used for fabrication of PLD thin films of ruby is shown in Fig. 1. A second harmonic of Q-switched Nd:YAG laser (Quanta system model no. HYL-01), pulse duration of ~8 ns, was focused on to the ruby target mounted, inside the ablation chamber. The focusing of high fluence ~23 J/cm^2 resulted in the formation and expansion of plasma of the target material, and was deposited in the form of thin film on to the substrate (quartz and sapphire) placed at a distance of 5 cm away from the target. All the samples of PLD ruby thin films were deposited in a background pressure of around 2×10^{-3} mbar of oxygen gas. Thin films were deposited for 2 h and 4 h on quartz substrate at room temperature and also for 1 h at 650 °C substrate temperature. The 4 h deposited sample was annealed for 2 h at 1000 °C. On sapphire substrate, ruby thin films were grown for three different deposition time; 30 min, 1 h and 2 h at 650 °C substrate temperature. These samples were annealed at 1000 °C for 2 h. Table 1 lists the details of all the PLD deposited thin films of ruby. The maximum deposition rate observed was 2.16 nm/min on sapphire substrate. The thickness of the deposited films were measured by Veeco Dektak 150 profilometer and listed in Table 1. The emission and excitation spectra of the PLD thin films were recorded by using Edinburg, FS-920 P fluorimeter. The samples were excited using 532 nm light from a Xenon lamp. The fluorescence lifetime measurement was performed by using a micro second flash lamp of fluorimeter. Raman spectra were recorded by Horiba Jobin Yvon, LabRam HR800 micro-Raman spectrometer using 488 nm of argon ion laser. Temperature dependent PL spectra measurement was carried out, in the range 138–473 K, by low temperature Linkam stage, THMS 600 integrated with LabRam having a resolution of 0.2 cm^{-1}, using 632.8 nm He:Ne laser as the excitation source.

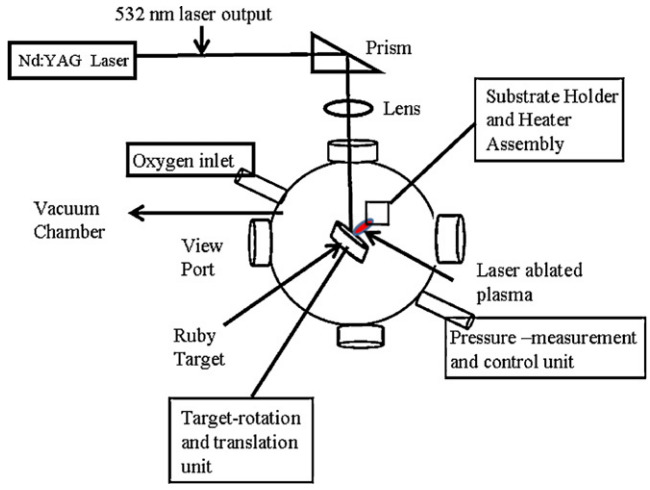

Fig. 1. Schematic of pulsed laser deposition setup.

3. Result and discussion

3.1. Characterization of pellets

The intense red confocal image of one of the pellet (0.5 wt% of Cr_2O_3), on excitation with 543 green He–Ne lasers, is shown in Fig. 2(a) confirming the ruby phase. HRTEM image from the pellet is shown in Fig. 2(b), the measured d-spacing of 0.261 nm further confirmed the ruby phase [25]. Raman spectra of alumina and chromium oxide powder, used to prepare the pellet and the sintered pellet are shown in Fig. 3. Absence of any well-defined band in the Raman spectrum of alumina indicated the γ-Al_2O_3, which is Raman inactive [26]. Fig. 3(b) shows the Raman bands of commercial chromium oxide powder (Cr_2O_3) used for the pellet. The observed bands at 306.2, 342.7, 390.6, 541.2, 597.8 and 670.6 cm^{-1} are in agreement with the Raman bands of Cr_2O_3 [27]. The Raman bands of sintered pellet (0.5 wt% of Cr_2O_3) are shown in Fig. 3(c). The observed Raman bands are located at 341.2, 352.7, 381.4, 417 and 645.8 cm^{-1}. The Raman bands at 381.4, 417.5 and 645.8 cm^{-1} corresponds to the corundum phase [27,28]. The LO band at 417.5 cm^{-1} in the pellet is signature of ruby phase [28]. Fig. 4(a) and (b) shows the excitation and emission spectra of ruby pellets for three different chromium concentration 0.05 wt%, 0.5 wt%, and 1.0 wt% of Cr_2O_3 in Al_2O_3. Two broad absorption bands centered at 402 and 554 nm in Fig. 4(a) correspond to the blue and green absorption bands of ruby. These bands at 402 and 554 nm are associated with the spin-allowed transitions from the $^4A_2$ ground state to the $^4F_2$ excited state (U-band) and to the $^4F_1$ excited state (Y-band) respectively as shown in Fig. 5. The weak, sharp B lines in absorption states, Fig. 4(a) are associated with the spin-forbidden transition to the doublet levels [1]. These are between states of the same crystal-field orbital configuration and take place through single-electron spin flips. Fig. 4(b) shows the photoluminescence spectra of ruby pellet consisting of well resolved R_1 and R_2 lines at 694.2 and 692.7 nm respectively. In ruby, this bright red light emission results from