Laser induced nano structured periodic patterns in ferroelectric bismuth vanadate thin films

G. PARAMESH, N. KUMARI*, S. B. KRUPANIDHI, K. B. R. VARMA
Materials Research Centre, Indian Institute of Science, Bangalore-560012, India

Bismuth vanadate ($Bi_2VO_{5.5}$) thin films were grown by pulsed laser deposition technique on corning glass substrates. The as deposited amorphous films were irradiated by pulsed Nd: YAG laser of 1064 nm wavelength as functions of angle of incidence and laser intensity. Irradiated areas were examined using polarizing microscope which revealed the existence of grating-like periodic structures. Periodicity was found to be close to that of the laser wavelength. The X-ray diffraction studies carried out on irradiated (at threshold power) films confirmed their crystalline nature. Periodic structures comprised of nano crystallites of 50 nm – 70 nm sizes. Formation of periodic structures was attributed to the interference effects arising due to surface scattered wave and the incoming laser beam.

(Received May 12, 2011; accepted July 9, 2011)

Keywords: Laser irradiation, Pulsed laser deposition, Bismuth vanadate, periodic structures

1. Introduction

Nonlinear interaction of high energy laser beam with the matter has been an exciting area of research as it unravels both scientifically and technologically important phenomena which could be exploited in the design and fabrication of useful optical devices. The possible effects as a result of high energy laser matter interaction could be the selective melting of the surface, ultra fast quenching, periodic energy deposition due to the interference of laser pulses, fast recrystallization etc. Accordingly, it would result in nanocrystallization, amorphous or glass formation, ridge formation and periodic structures depending on the nature of the materials (semiconductors, metals, polymers, or insulators), and the interacting laser's wavelength, pulse width (nano second pulse, femto second pulse or continuous wave), peak intensity and duration of irradiation [1, 2]. As the nonlinear interaction of laser changes the surface morphology, structure, refractive index, formation of periodic gratings; it is possible to modify and control the optical and the electrical properties of the surfaces of the bulk samples and thin films. Formation of periodic surface structures or ripple formation was the most common observation made by many authors on opaque and transparent surfaces using high energy nano or femto second lasers [3, 4]. In the process of nonlinear interaction of high intense laser pulses with matter, the changes may occur in the time scales of a few seconds, which is practically difficult to make in-situ observations. Most theories are developed depending on the experimental observations made on different kinds of materials. Laser induced periodic surface structures (LIPSS) or laser induced ripple deformation (LIRD) were observed on semiconductor surfaces such as Ge Si, metallic surfaces like Al and Brass [2-5] and in polymer films [6,7]. Our group has reported the formation of nanocrystalline grating like structures on borate and tellurite based glasses and glass nanocrystal composites [8, 9]. The laser interaction study with Perovskites and Aurivillius based ferroelectrics is scanty. Laser irradiation studies on the technologically important oxides may help in modifying/tailoring the physical properties of the films and surfaces. The present article aims at the experimental investigation of pulsed Nd: YAG laser (λ=1064 nm) interaction with bismuth vanadate $Bi_2VO_{5.5}$ (BVO) thin films obtained by pulsed laser deposition technique. The details of which are reported in the following sections. The optical and ferroelectric properties of the BVO thin films were reported else where [10].

2. Experimental

The polycrystalline $Bi_2VO_{5.5}$ (BVO) targets that were employed for the pulsed laser deposition of films were fabricated using the powders, synthesized via the conventional solid-state reaction route. For this purpose fine powders of high-purity (Aldrich Chemicals 99.9%) Bi_2O_3 and V_2O_5 with appropriate molar ratios were weighed and ball milled for 5h to obtain homogeneous mixture. The powders were then calcined at 800°C for 5 h. The calcined powders were cold pressed (80 kN in an 18mm diameter die) and sintered at 825°C for 8 h to form a single-phase (as confirmed by X-ray powder diffraction studies XRD) dense target. The resultant high-density targets were used for the deposition of films.

BVO thin films were deposited on Corning glass (Corning 7059) substrates using a KrF (Lambda Physik Compex 201, wavelength 248 nm) excimer laser with 10 ns pulse duration. The output laser beam was focused onto a rotating target at an angle of 45° by a UV lens associated with a focal length of 30 cm. The energy stability of the incoming beam was monitored using an external energy meter. Laser energy of 160 mJ/pulse was maintained constant during the deposition and the laser beam was focused to obtain a fluence of approximately 2.5 J cm^{-2} for all the samples under study. The base vacuum was maintained at 1×10^{-6} Torr. The optimization of the oxygen partial pressure was carried out and the films were deposited at the oxygen ambient pressure of 100 mTorr at room temperature. The X-ray powder diffraction studies were carried on BVO films using Cu Kα (1.541 Å) radiation (Bruker D8 Diffractometer). The as deposited amorphous (confirmed by XRD) films were irradiated with 10 ns pulse Nd: YAG laser (Spectra Physics, Lab 180) of 1064 nm wavelength at different laser intensities. Laser power was measured using energy/power meter (Newport, Energy meter 842 PE). Irradiation at different incident angles was carried out by mounting the sample on a rotation stage (Newport Rotation Stage SR 50). The surface features of the irradiated films were examined by means of an ex - situ contact mode atomic force microscope (AFM) (Veeco CP-II) and polarizing microscope (Olympus, BX51). The AFM images were obtained in the repulsive force regime with a force constant of 1.5 nN between the AFM tip and the sample surface. The optical constants (absorption coefficient and the refractive index) of the films were obtained by spectroscopic ellipsometry (SENTECH 850, SENTECH Instruments).

3. Results and discussion

The as deposited BVO thin films on glass substrates at room temperature were confirmed to be amorphous by XRD studies (Fig.1). These amorphous films were irradiated (normal incidence) with pulsed Nd: YAG laser (pulse width 10 ns and 10 Hz repetition rate, 8mm beam diameter) at various laser fluencies (400 mJ/cm^2- 900 mJ/cm^2). The irradiated films were examined through optical microscope. At laser fluence of 700 mJ/cm^2 (threshold fluence), periodic grating-like structures were noticed. Optical micrograph obtained for the irradiated BVO films are shown in Fig.2.

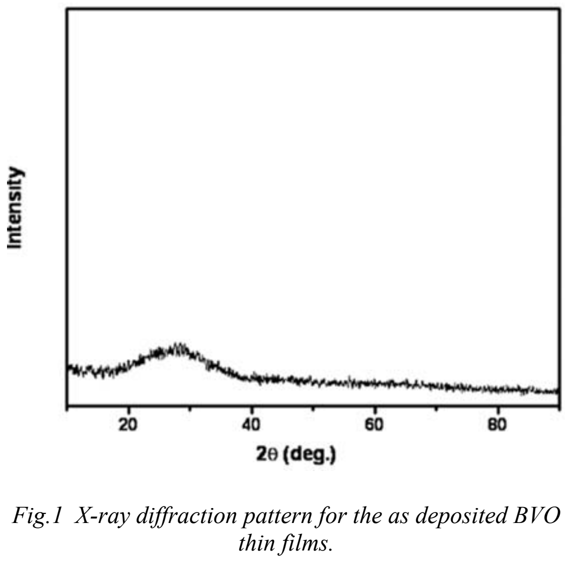

Fig.1 X-ray diffraction pattern for the as deposited BVO thin films.

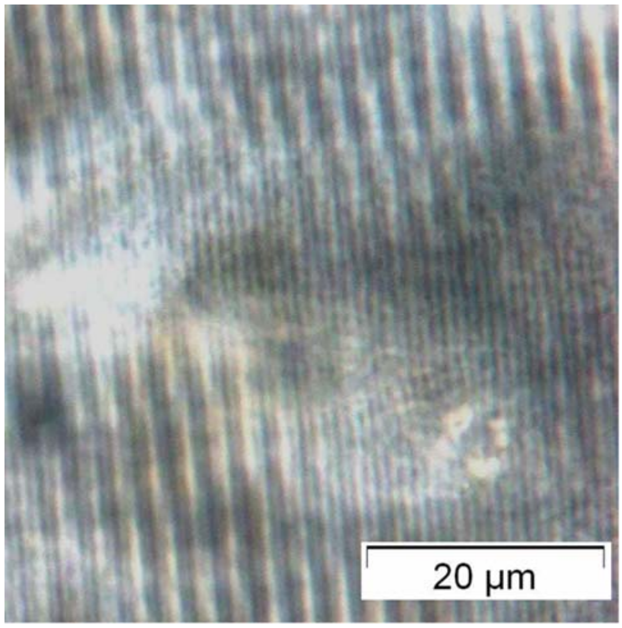

Fig.2 Optical micrograph of irradiated BVO films at threshold laser intensity.

One could realize the presence of grating-like periodic structures in this micrograph. The periodicity of the pattern is around 1µm which is close to the incident laser wavelength (1.064 µm). This periodic structure formation is attributed to the interference effects arising from the incoming laser beam and surface scattered waves parallel to the surface [13, 14]. To visualize the influence of the angle of incidence on the pattern formation and its periodicity, the irradiation studies were carried out at various angles of incidence and the resultant optical micrographs are depicted in Fig.3 (a to d) for the angles of incidence 15^0, 30^0, 45^0, and 60^0 respectively.

The fringe spacing (Λ) of the periodic patterns was found to be in accordance with the formula [2]

$$\Lambda = \frac{\lambda}{\cos\theta}$$

where λ is the wavelength of the laser, and θ is the incident angle. The variation of the fringe spacing with the angle of incidence is depicted in Fig.4.

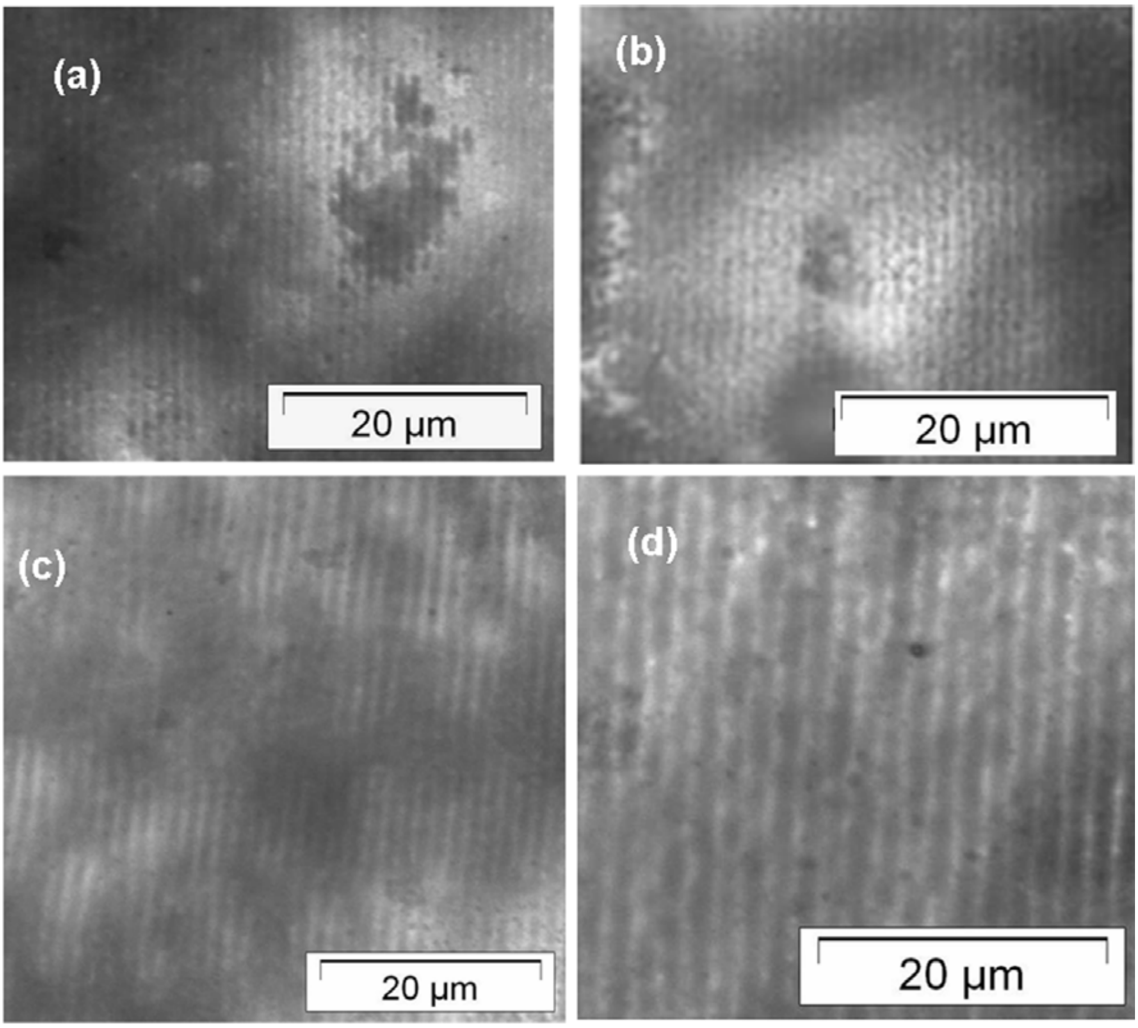

Fig.3 Periodic structures at different angle of incidence (a) 15^0, (b) 30^0, (c) 45^0, and (d) 60^0

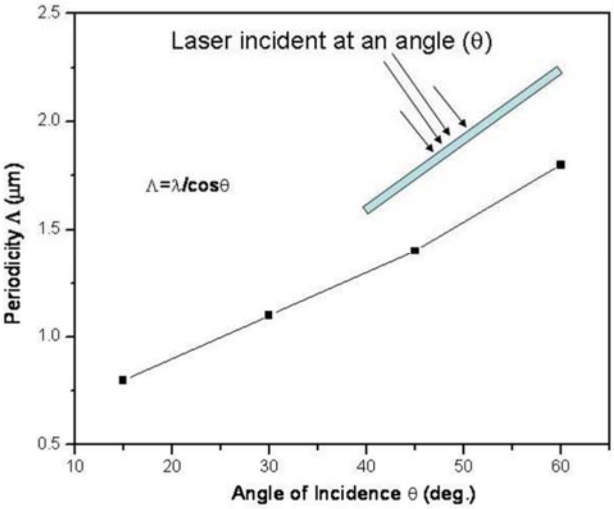

Fig.4. Variation of periodicity with the angle of incidence of the laser beam.

The fringe spacing (Λ) increases with the increase in angle of incident beam. As the periodicity of the laser inscribed grating is ~1 μm, this corresponds to a fine grating ruled with 10,000 lines/cm.

The irradiated films were subsequently investigated for their structures using X-ray diffraction and found to be crystalline (Fig.5). The broad and sharp intense peaks indicate their nanocrystalinity. The observed Bragg peaks at 2θ angles 27^0 and 55^0 indexed as (113) and (119) plane ,respectively to the orthorhombic phase of $Bi_2VO_{5.5}$. The micro laser Raman spectra obtained for the laser irradiated region is shown in Fig.6.

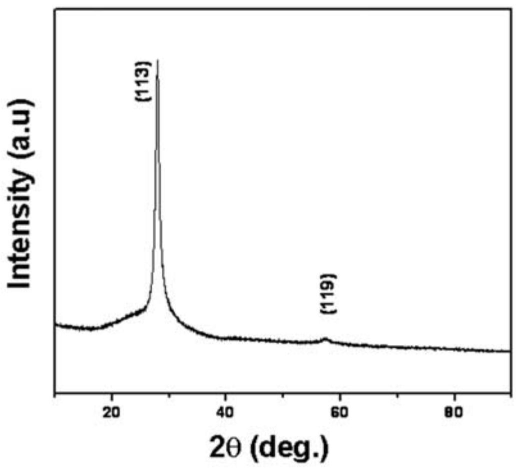

Fig.5 X-ray diffraction pattern for BVO films subsequent to laser irradiation.

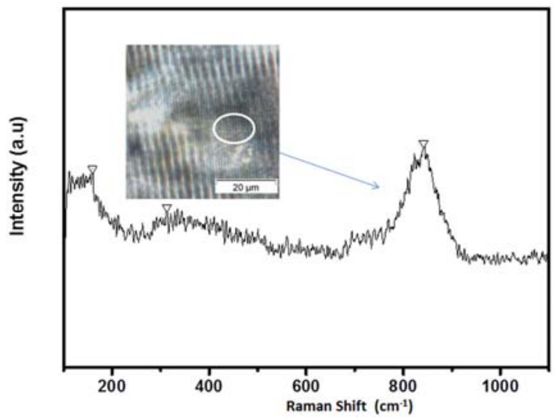

Fig.6 Raman Spectra of the irradiated BVO films.

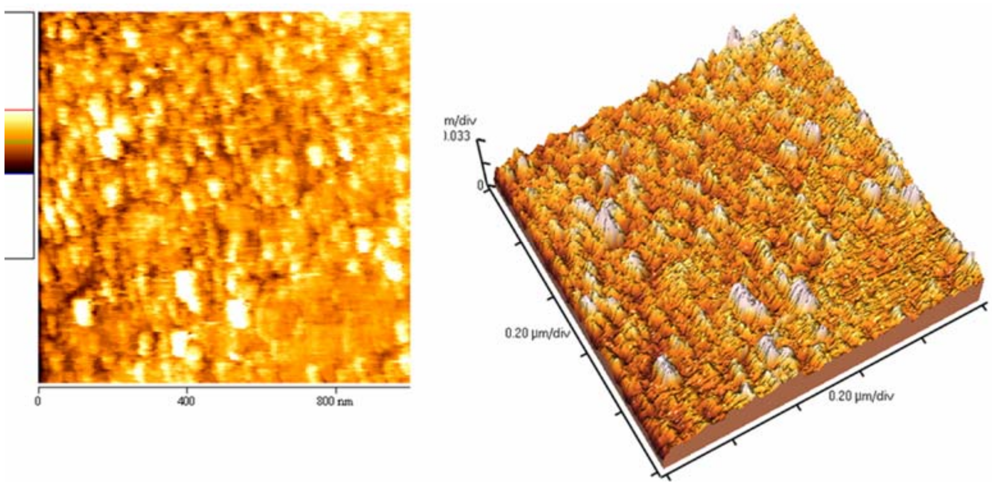

Fig.7 AFM image of irradiated BVO film (at the threshold laser power, crystallite size 70 nm)

The periodic structures were focused to record Raman spectra. The characteristic intense band is observed at 842 cm^{-1}. This is ascribed to the symmetric V-O stretching modes of the VO_4 tetrahedra which are regularly arranged in bismuth vanadate structure. The other weak band at 342cm^{-1} is assigned to the bending modes of the VO_4 tetrahedra [11]. These Raman spectroscopic observations are in consistence with the reported $Bi_2VO_{5.5}$ phase [12]. Atomic force microscopy was used to find the crystallite size of the irradiated films (Fig.7).

The average crystallite size is about 70 nm. At higher fluence levels, the periodic patterns were not encountered (not reported here) owing to much higher temperatures associated with them and as a result, the sub surface layer would get ablated continuously leading to the formation of smooth surface.

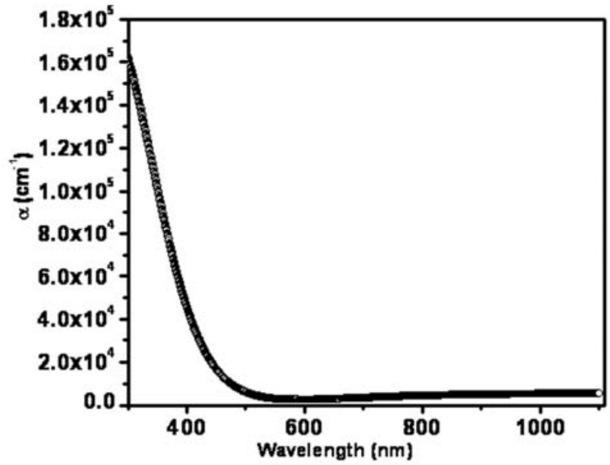

Fig.8 Absorption coefficient (α) vs. wavelength (λ) for the as deposited BVO films.

The crystallization of BVO films on laser irradiation is rationalized by invoking photo thermal effects. The incident laser pulses that were absorbed partially by the BVO film generate heat which would enhance the surface temperature. If the period between the pulses is shorter (as in the present case) than cooling time, multi pulse effect will accumulate the energy to raise the temperature as the thermal conductivity of the BVO is relatively low. Subsequently the local material melting or evaporation (ablation) may take place depending on the amount of temperature rise after certain number of pulses. Indeed the rise in temperature at the surface was determined using the following formula [15]

$$T_{th}^{\max} = T_0 + \frac{F_{th}\alpha_{th}}{\rho c_v}$$

where T_{th}^{max} is the maximum temperature at threshold, T_0 is room temperature F_{th} is threshold laser fluence, α_{th} is absorption coefficient, ρ is density and c_v is volume specific heat of the BVO. Absorption coefficient (α) as a function of wavelength of light for BVO films prior to laser irradiation is shown in Fig.8. For F = 775 mJ/cm^2, α = 5.235X10^{3}cm^{-1}, c_v = 1.5 J/gm.K and ρ =7.38 gm/cm^3 [16], the rise in temperature obtained using above formula is 396.5 K. The temperature rises further due to deposition of subsequent pulses so that crystallization of the BVO films takes place. The total number of pulses is 300.

5. Conclusions

Amorphous BVO thin films were irradiated by Nd:YAG laser (λ=1064 nm) at various incident angels. Formation of grating-like structures was observed. Periodicity was found to be of the order of wavelength of the laser used. The periodic structure formation was attributed to the interference effects on the surface of the film. Irradiated films were found to be crystalline in nature associated with the crystallite size of about 70 nm.

References

[1] V.I. Emel'yanov, Laser Phys**.** **2**, 389 (1992).
[2] Jeff F.Young, J.S.Preston. H.M.van Driel, J. E.Sipe, Phy. Rev. B **27**(2), 1155, (1983).
[3] M.A.Vasylyev,M.M.Nischenko, V.A. Tinkov at.el., Appl.Surf.Sci.**255**, 1712 (2008)
[4] V.I.Emel'yanov, D.V.Babak, Appl.Phys.A **74**, 797-805 (2002)
[5] M.J.Soileau, IEEE J. Quantum Electron. **20**, 464 (1984)
[6] V.I.Vlad, A.Petris, V.N.Chumash, I.Cojocaru Appl.Sur.Sci **106**, 356 (1996)
[7] M.Csete, O.Marti and Zs.Bor Appl.Phys.A **73**, 521 (2001)
[8] B.Harihara Venkataraman, N.Syam Prasd, K.B.R.Varma Appl.Phys.Lett. **87**, 091113 (2005)
[9] Niyaz Ahamad Madhar K.B.R.Varma, J.Ame.Ceram.Soc. **92** (11), 2609 (2009)
[10] N.Kumari, S.B.Krupanidhi and K.B.R.Varma, Appl.Phys.A. **91**, 693-699 (2008)
[11] Hardcastle, F. D.; Wachs, I. E.; Eckert, H.; Jefferson, D. A. J. Solid State Chem., **90**, 194 (1991)
[12] D. Barreca, L. E. Depero, V. Di Noto, G. A. Rizzi, L. Sangaletti, and E. Tondello, Chem. Mater**.,** **11**, 255-261(1999**)**
[13] Anthony E.Siegman, and Philippe M.Fauchet IEEE J.Quantum Electron. **22**(8),1384 (1986)
[14] Jeff F.Young, J.E.Sipe and H.M.van Driel, Phy. Rev. B **30**(4), 2001 (1984)
[15] P.E.Dyer, R.J.Farley, R.Giedl, D.M.Kamakis, Appl.Surf.Sci, **96**, 537 (1996)
[16] K V R Prasad, K B R Varma, J.Phy.D.Appl.Phys. **24**, 1858 (1991).

*Corresponding author: neelamk99@gmail.com