Irreversible thermochromic response of RF sputtered nanocrystalline BaWO₄ films for smart window applications

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We report irreversible thermochromic behaviour of BaWO₄ (BWO) films for the first time. BWO films have been deposited at different substrate temperatures (RT, 200, 400, 600 and 800 °C) using RF magnetron sputtering in pure argon plasma. BWO films deposited at 800 °C exhibit crystalline nature. Also, BWO films deposited in the temperature range of 400 - 600 °C exhibit WO₃ as a secondary phase and its weight percentage decreases with an increase in deposition temperature, whereas the films deposited at 800 °C exhibited pure tetragonal phase. FESEM images revealed that as the average particle sizes of the films are higher as compared with the thickness of the films and is explained based on Avrami type nucleation and growth. The transmittance of the films decreases with an increase in deposition temperature up to 600 °C and increases thereafter. Films deposited at 600 °C show ≤ 20% transmittance, looking at the films deposited at room temperature and 800 °C exhibits 90 and 70%, respectively. The refractive index and extinction coefficient of the films show profound dependence on crystallinity and packing density. The optical bandgap of BWO films increases significantly with an increase in O₂% during the deposition. The optical bandgap of the BWO films deposited at different temperatures in pure argon plasma, are in the range of 3.7 to 3.94 eV whereas the films deposited at 600 °C under different O₂ plasma are in the range of 3.6 - 4.5 eV. The formations of colour centres are associated with the oxygen vacancies, which are clearly seen from the optical bandgap studies.

The observed irreversible thermochromic behaviour in BWO films is attributed to the presence of oxygen vacancies that arises due to the electrons trapped at oxygen vacancies causing an inter valence charge transfer of W⁵+ to W⁶⁺ and is confirmed through the change in the optical density (ΔOD). Further, the Raman spectra are being used to quantify the presence of oxygen vacancies and the formation of pure BWO phase. The obtained optical responses of BWO films are promising for solar cell and smart window applications. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4935068]

I. INTRODUCTION

Microwave dielectric materials have been studied intensely due to their promising applications in various wireless communication devices. The requirements of the material to be used in above applications are low loss tangent (tanδ), moderate dielectric constant (εr) and temperature stability of resonant frequency (τf) close to zero. BaWO₄ (BWO) is one of the promising microwave materials, which has been widely used in microwave and electro optic applications due to its excellent microwave dielectric properties: εr of 12, Q × f₀ > 50 THz and a τf of -33 ppm/ °C.¹,² However, most of the studies on BWO are focussed on the microwave dielectric properties in bulk form.

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Recent past, oxide films exhibit thermochromic response are extensively investigated due to their wide applications in smart windows, gasochromatic sensors, displays to block the infrared radiation, and in solar cell applications. Thermochromism arises due to the changes in optical properties with change in deposition temperature and is seen in a large number of compounds. The films change their optical response (non-reversible color changes on heating) with the substrate temperature. Because the variation of temperature is one of the easiest approaches of aiming to change the nature of materials, it is appropriate to use the observation of thermochromism, particularly in the visible range. The thermal behaviour of the different materials may be divided into two divisions one exhibits non-reversible thermochromism over a wide temperature range, and the other displays a sharp interchange in optical properties at a particular temperature. The non reversible thermochromism can be used as protective layers and window color coatings. Nevertheless, there are very few studies available on BWO thin films and there is no report available on irreversible thermochromic nature of BWO films. Pontes et al. studied structural and optical properties of BWO films by prepared by chemical route. Dinesh et al. demonstrated the growth of crystalline BWO films at room temperature and reported structural and microstructure of these films. Cho et al. obtained highly crystallized BWO films at room temperature by using electrochemical method. However, irreversible thermochromic behaviour was not observed in BWO films prepared by the above methods. Moreover, most of the studies were focussed on the room temperature crystallization of BWO films. Further, it is known that the properties of the films depend on the deposition technique. Also, the systematic study on optical properties and growth of BWO films using RF plasma has not been studied earlier. In the current study, we report the growth of BWO films at different substrate temperatures using RF reactive magnetron sputtering technique. The significance of this study is to demonstrate irreversible thermochromic response and optical properties of BWO films for the first time.

II. EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

BWO sputtering target was prepared using the mechanical alloying method. The high-purity powders of BaCO$_3$ (99.99%), WO$_3$ (99.99%) were used as starting materials and were weighed in accordance with their stoichiometry. The weighed powders were ball milled at 300 rpm for 60 h with tungsten carbide vial and balls using planetary ball mill (Pulverisette, Fritsch GmbH, Germany). It was found that the pure BWO phase is obtained for the samples milled for 60 h. Subsequently, the milled BWO powders were pressed into a cylindrical target of 62 mm in diameter with 3 mm in thickness and sintered at 800 °C for 3 h. The BWO thin films were deposited by RF magnetron sputtering on amorphous SiO$_2$ substrates at different substrate (RT, 200, 400, 600 & 800 °C) temperatures under pure argon plasma. The deposition was carried out for 3 h at a fixed RF power of 40 W. The deposition chamber was pumped down to a base pressure of 1.0 × 10$^{-6}$ Torr and the sputtering pressure of 5 × 10$^{-3}$ Torr is maintained constantly throughout the deposition process.

The phase purity of sintered BWO sputtering target was examined by recording the XRD patterns using X-ray diffractometer (Rigaku, TTRAX – III) with CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å) and the crystallinity of the BWO thin films at different substrate temperatures are evaluated using the XRD patterns obtained using a X-ray diffractometer (PAN analytical, X’pert) with CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å). The X-ray diffraction pattern of sputtering target prepared by mechanical alloying was refined by considering I$_{41}$/a space group using Rietveld refinement technique and fullprof program. Surface morphology of BWO films was examined by field emission scanning electron microscope (FESEM, Sigma Zeiss). Spectral transmission characteristics in the wavelength range 200 - 800 nm were measured using a UV - VIS - NIR spectrophotometer (UV 3101PC, SHIMADZU). The optical constants and bandgap are calculated using the envelope and Tauc methods, respectively. The Raman spectra of BWO thin films obtained using an Ar$^+$ laser with an excitation at 633 nm source at RT are acquired by Laser Micro Raman System (Horiba Jobin Yvon, LabRam HR).

III. RESULTS AND DISCUSSION

The phase formation of the BWO ceramics occurred after milling for 60 hours. The XRD pattern of BWO target along with the Rietveld refinement data of the sputtering target, sintered at 800 °C.
for 3 hours is shown in Fig. 1(a). BaWO$_4$ ceramics revealed the tetragonal system with I$_{41/a}$ space group. The refinement is carried out by considering I$_{41/a}$ space group. The lattice parameters, atomic positions of the Ba, W, and O atoms, and occupancy are refined. The corresponding lattice constant values are found to be $a = b = 5.6102$ Å, $c = 12.7101$ Å, which are in agreement with earlier reports [JCPDF file # 850588]. The fitting parameters are: (i) $\chi^2 \approx 7.68$, (ii) $R_{Brag}$ factor $\approx 5.091$ and (iii) $R_f$ factor $\approx 5.410$.

BWO thin films deposited on amorphous SiO$_2$ substrates, at different substrate temperatures deposited in pure argon plasma are shown in Fig. 1(b). It is observed that BWO films deposited both at an ambient temperature, and 200 °C depicted amorphous nature. As the deposition temperature increases, the films exhibit crystalline nature and the intensity of the peaks increased gradually. In general, oxide films grow in amorphous phase at ambient temperatures due to insufficient thermal energies and lattice mismatch between substrate and the film. At higher deposition temperatures, the thermal energy facilitates the atoms to find minimum energy sites, which assist the nucleation of microscopic crystals into large grains. BWO films deposited at 400 °C and 600 °C displayed WO$_3$ as a secondary phase. The major diffraction peaks observed for WO$_3$ phase are (2 0 0) and (0 2 0) at $2\theta = 24.19$ and $23.77$ indicate that WO$_3$ exhibit an orthorhombic structure [JCPDF file # 710131] for the films deposited at 400 °C and 600 °C, respectively. In the presence of WO$_3$, the signatures of the (2 0 0) and (0 2 0) reflections disappear in the films deposited at 800 °C. BWO films deposited at 800 °C showed a pure tetragonal phase without any secondary phase. The formation of WO$_3$ is natural, because it needs lower thermal energy as compared to BWO. The average crystallite sizes of films are calculated by using the Scherrer’s formula and are in the range of 33.6 - 51.75 nm, which confirms the formation of nanocrystalline films. Further to quantify the presence of WO$_3$ and BWO phases, the weight ratios of orthorhombic (WO$_3$) and tetragonal (BWO) phases for the films deposited at 400 °C and 600 °C, are calculated using the following expression

$$W_{WO} = \{1/[1 + 1.265(I_{BWO}/I_{WO})]\} \times 100$$

where $W_{WO}$ denotes the weight fraction of the orthorhombic phase, $I_{BWO}$ and $I_{WO}$ are the intensity of tetragonal phase and orthorhombic phase, respectively. The weight fraction of the orthorhombic phase decreases from 20.81% to 8.34% with an increase in deposition temperature from 400 °C to 600 °C and subsides completely in the film deposited at 800 °C. XRD patterns of the BWO films deposited at 600 °C with different oxygen plasma were shown in Fig. 1(c). The BWO films deposited under pure argon plasma displayed a mixture of WO$_3$ and BaWO$_4$ phases. With an increase in O$_2$% from 50% to 100% in the deposition chamber, the secondary phase vanished completely and the crystallinity of the BWO films enhanced by an increase in O$_2$%.

FESEM images of the BWO films deposited at different substrate temperatures are depicted in Fig. 2. It is interesting to note that even the films deposited at ambient temperature show significant features. The average grain size of the films increases with a rise in substrate temperature and the film deposited at 800 °C exhibits abnormal grain growth. The average grain sizes of the films found to be 326, 361, 453, 536 and 784 nm for the films deposited at RT, 200, 400, 600 and 800 °C, respectively. All the deposited films have the same thickness of 450 ±10 nm. Further, it is significant to note that the average particle size of the films is higher as compared to the thickness of the films and this can
be explained on the basis of Avrami type nucleation and growth. The thermal energy available on the surface of the substrate facilitates the particles to be nucleated continuously throughout the film with the termination caused by the impingement of neighbouring particles growing at a steady rate.8,9

The spectral transmittance spectra of nanostructured BWO thin films deposited at different substrate temperatures along with their photographs are shown in Fig. 3(a). The transparency of BWO film, deposited at room temperature is about 90%. As the deposition temperature increases, the transparency of the film reduces to 70%; this shows the evidence of thermochromic nature in BWO films. In addition, there are two regions, where a transparent oscillating region and a region of strong absorption. All the transmission spectra of BWO films above 420 nm exhibit peaks and valleys that are associated with the reflections from the incident light from the air - film, and film - substrate tends to interference effects. The strong absorption observed below 400 nm and the absorption edge of the films exhibited a red shift, which shows the effect of crystallinity in the deposited films. Temperature dependence of refractive index and packing density is shown in Fig. 3(b). It is observed that both the refractive index and packing density of the films follow the similar trend as a function of temperature that shows the dependence of refractive index on packing density of the films. Further, the refractive indices of the films are higher for the films deposited in the temperature range of 400 to 600 °C, this may be to due to the appearance of mixed phases. Films deposited below 400 °C, show lower refractive
indices, which are attributed to the microscopic packing densities and low adatom mobilities of the films. The obtained refractive index values are in the range of 1.76 - 2.1 @ 600 nm and are comparable with the reported values.\textsuperscript{16,17} The variation in extinction coefficient and optical bandgap as a function of deposition temperature is depicted in Fig. 4(a). The extinction coefficient of the films increases progressively with an increase in deposition temperature. The enhancement in crystallinity, packing density and average grain size of the deposited films causes more scattering of incident light as a result the extinction coefficient increases. The optical absorption edge of the films deposited at different substrate temperatures are shown in Fig. 4(b). The optical bandgap of the films decreases linearly with an increase in deposition temperature upto 600 °C and increases slightly thereafter. The decrease in optical bandgap and simultaneous increase in the extinction coefficient is attributed to the occurrence of thermochromism in BWO films. The slight increase in bandgap above 600 °C is attributed to the phase pure BWO, because WO\textsubscript{3} has the lower optical bandgap as compared with BWO.\textsuperscript{7,18} The obtained optical bandgaps of BWO films deposited under different substrate temperatures are in the range of 3.7 to 3.94 eV. Further, to see the effect of O\textsubscript{2}% on the optical bandgap, BWO films are deposited under different O\textsubscript{2}% (25, 50, 75 & 100%) at 600 °C and their transmittance spectra’s and absorption edges are shown in Fig. 5(a) and 5(b), respectively. It is clearly seen that the films show higher transmittance and larger bandgap values. Also, with increase in O\textsubscript{2}%, the optical bandgap of films increased significantly from 3.6 to 4.5 eV. The variations in the optical bandgaps can be attributed to the presence of oxygen vacancies. Further, to quantify the presence of oxygen vacancies, the change in optical density (\(\Delta OD\)) is calculated and this is proportional to the amount of created colour centres. \(\Delta OD\) is calculated using the following expression

\[
\Delta OD = \log_{10}(T_b/T_c)
\]
FIG. 6. (a) The change in optical density as a function of wavelength and (b) The variation in optical density as a function of substrate temperature for different wavelengths.

where $T_b$ and $T_c$ are transmittances before and after coloration, respectively. The change in $\Delta OD$ as a function of wavelength is shown in Fig. 6(a). It is observed that $\Delta OD$ decreases with an increase in temperature, which shows the increase in colour centres. Further, the variations of $\Delta OD$ as a function of substrate temperature measured at different wavelength are shown in Fig. 6(b). It is observed that the change in $\Delta OD$ decreases both with increase in substrate temperature and the wavelength.

The reduction in transmittance with increasing deposition temperature can be described as follows: the higher deposition temperature intensifies the kinetic energy of the adatoms and surface mobility, which results in larger grain sizes and better crystallinity, and is evident from FESEM images (Fig. 2). The enhanced grain size scatters the light, which results lower transmittances. Further, to understand the variations in transmittance, we have measured the resistances of the deposited films and are in the range of 0.9 to 5.2 giga Ohms. We found that the resistance of the films decreases with an increase in deposition temperature and showed a lowest value at 600 °C, this shows the variations in the transmittances can be attributed to the oxygen vacancies, which complements the BWO films deposited at different $O_2$% (See Fig 5(a) and 5(b)). It is well known that the optical bandgap of oxide films depends on oxygen partial pressure / vacancies, and it is indirect estimation of stoichiometry. As the oxygen percentage increases in the deposition chamber, the films will grow in stoichiometric state as a result the optical bandgap of the film increases, and the obtained optical bandgap values are slightly lower than the values reported by Zawawi et al, for the pure BWO nanopowders prepared in sucrose - template method. Also, these calculated bandgap values are comparable with BWO nanoparticles ($E_g \sim 4.1$ eV) prepared by the modified combustion process.

From the above observations, it can be infer that the absorption edges of the films shifts towards lower energy side with an increase in deposition temperature, which is attributed to the increase in crystallinity and coloring effect. At 600 °C, the shift in absorption edge towards lower energies may be due to the increase of energy for the charge transfer from oxygen to tungsten. As a result, the density of state at the top of the band decreases, whereas the density of states at the conduction band increases.

The similar response was observed for the WO$_3$ films and it is well known that the themochromic response in these films achieved by vacuum heating while bleaching is obtained after annealing in air. For BWO films deposited at 600 °C, W$^{6+}$ prefers lower oxidation states due to the release of oxygen as a result it deviates from the stoichiometric state. The observed variations in the optical bandgap can be attributed to a small polaron transition between W$^{6+}$ and W$^{5+}$ or W$^{5+}$ and W$^{4+}$. This inert valence can be described by the following expressions:

$$hv + W^{5+} (A) + W^{6+} (B) \rightarrow W^{6+} (A) + W^{5+} (B)$$

$$hv + W^{5+} (A) + W^{4+} (B) \rightarrow W^{5+} (B) + W^{4+} (A)$$

Furthermore, the presences of created colour centres are quantified by calculating the change in $\Delta OD$ that estimates the presence of oxygen vacancies in the deposited films. Various mechanisms were
FIG. 7. Raman spectra of BWO thin films deposited on amorphous SiO$_2$ substrates at different substrate temperatures.

proposed to explain the thermochromic response in various materials.\textsuperscript{6,26,27} But, in the present study, the achieved irreversible thermochromic behaviour in BWO films is attributed to the oxygen vacancies.

Further to quantify the presence of oxygen vacancies in the BWO films, Raman spectra for the films deposited at different substrate temperatures are displayed in Fig. 7. The identified internal (927.03 - 923.27, 705, 213 cm$^{-1}$) and external (130 cm$^{-1}$) modes for the BWO films deposited at 400°C, 600°C and 800°C are in consistent with the earlier reports.\textsuperscript{28,29} The obtained vibrational modes in Raman spectra of BWO films can be divided into two groups, internal and external. The internal vibrations correspond to the oscillations inside the [WO$_4$]$^{2-}$ molecular group with an immovable mass center. The external or lattice phonons correspond to the motion of the Ba$^{2+}$ cation and the rigid molecular unit.\textsuperscript{30} Raman spectra of the BWO films deposited at RT, and 200°C revealed amorphous nature. Fig. 7 demonstrates all the vibrational modes corresponding to the BWO films deposited at ≥ 400°C. Further, three modes connected to WO$_3$ are observed at 260 cm$^{-1}$, 321 cm$^{-1}$ and 801 cm$^{-1}$. The modes appeared in the low-frequency region (260 cm$^{-1}$, 321 cm$^{-1}$) are due to the bending vibration of $\delta$ (W$^{6+}$ - O), and the mode presented at the high – frequency (801 cm$^{-1}$) region can be assigned to the stretching vibration of $\nu$ (W$^{6+}$ - O).\textsuperscript{31–33} The intensities of the vibrational modes related to WO$_3$ increased with a rise in deposition temperature from 400°C - 600°C and diminish at 800°C, which indicates the formation of pure BWO phase. Furthermore, the full width at half maximum of the peak improves with an increase in deposition temperature. It is interesting to note that as the deposited temperature increases from 400°C to 800°C, the prominent internal mode appeared at 927.03 cm$^{-1}$ is shifted to 923.27 cm$^{-1}$ that demonstrate the formation of pure BWO phase, and these effects complemented the results obtained by XRD. This internal mode shift from 927.03 cm$^{-1}$ to 923.27 cm$^{-1}$ arises due to the formation of more tungsten ion concentration as compared to oxygen, which represents larger oxygen vacancies.\textsuperscript{34}

Further, BWO exhibited pure phase for the films deposited at 800°C, and it is significant to note that even pure BWO films also exhibited the irreversible thermochromic nature, and it changes its colour from transparent to pale yellow after a cycle from RT to 800°C. For this purpose a study of the temperature dependence of transmittance of this film’s gains importance, which is the subject matter of a future study.

IV. CONCLUSIONS

Irreversible thermochromic response in RF sputtered nanocrystalline BWO films observed for the first time. The impact of deposition temperature on structural, microstructural and optical properties of BWO films were studied systematically. The optical bandgap of the BWO films deposited at different temperatures in pure argon plasma, are in the range of 3.7 to 3.94 eV whereas the films deposited
at 600 °C under distinct O₂ plasma are in the range of 3.6 - 4.5 eV. The observed thermochromic behavior in BWO films was attributed to the presence of oxygen vacancies due to electrons trapped at oxygen vacancies causing an inter valence charge transfer of W⁵⁺ to W⁶⁺ in coloured BWO and is confirmed through the change in AOD. The Raman spectra of BWO films deposited at 800 °C exhibit pure BWO vibrational modes and this study compliments the obtained XRD results. The obtained response of BWO films was suitable for decorative and smart window applications.

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