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Optical constants of pulsed RF magnetron sputtered nanocolumner V_2O_5 coating

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ABSTRACT

Vanadium pentoxide (V_2O_5) coatings on quartz and Si(111) substrates are grown by pulsed RF magnetron sputtering technique at constant RF power of 700 W at room temperature. Phase, microstructure and surface morphology are investigated by X-ray diffraction, field emission scanning electron microscopy and atomic force microscopy techniques, respectively. The transmittance and reflectance spectra are recorded for the solar region (200–2300 nm) of the spectral window. Further, optical constants viz. optical band gap, refractive index and extinction coefficient of the deposited V_2O_5 coatings are estimated. Thickness dependent optical band gaps are found in the range of 2.78–2.59 eV. Wavelength dependent characteristic is also observed both for refractive index and extinction coefficient. Finally, thickness of the present coating predicted theoretically which is matched well with the thickness measured by direct measurement e.g., nanoprofilometry technique.

1. Introduction

Both for present and futuristic cutting edge technological applications, the uses of phase change materials (PCMs) are essential. One of the popular PCMs is vanadium oxide which show reversible behavior in both thermochromic and electrochromic transitions. Different oxides of vanadium posses metal to insulator transition (MIT) referred as Mott transition [1]. Basically Magneli (V_nO_{2n-1}) series oxides of vanadium viz. V^{2+}, V^{3+}, V^{4+} etc. (except V_7O_{13}) show aforesaid smart transition behavior where a drastic change in thermo-optical and electrical properties can be obtained beyond an applied critical temperature or voltage. Further, recent report [2] clarifies the debatable issue regarding phase transition of V_2O_5 as well. In fact, three groups [2–4] including the present authors [2] are also observed reversible phase transition in the film of V_2O_5.

Aforesaid phase change property makes vanadium oxide a promising material for optical applications e.g., for optical switching and optical shutter, in both electrochromic and thermochromic devices [5–7]. Therefore, it is indeed important to know the optical properties and optical constants of vanadium oxide. Although, there are several reports (Table 1, [2,5–23]) available regarding optical properties and optical constants of V_2O_5 however these information are neither systematic and nor comprehensive. These diversities in optical properties depend on processing techniques, surface roughness, thickness and substrate influences etc. as summarized in Table 1. Transmittance behavior of V_2O_5 is studied with varying thickness [2,5–23] in comparison to the thicker coating of V_2O_5 [7,8,13,14]. Ultra thin film (21 nm [2]), thin films (100–150 nm [5, 16]) and thick film (1000 nm [8]) show a high transmittance value (e.g., ~90%) in spite of significant difference in thickness. Benmoussa et al. [8], Soud et al. [20], and Aly et al. [21] report indirect band gap for the V_2O_5 films/coatings whereas others report direct (either allowed or forbidden) band gap for the same [2,6, 7,10–18, 23]. Further, very large band gap e.g., ~2 eV to ~3 eV of V_2O_5 is reported in literature [2,6,9, 19]. Similarly, high refractive index (~2.5) [8] and low refractive index (~1.85) [11] of V_2O_5 is reported. The range of extinction coefficient also varies from as low as 0.01 to as high as 0.2 [12, 17, 22].

Hence, from the aforesaid detailed literature survey presented in Table 1, it is evident that the systematic and in-depth studies are not available for the optical behavior and in particular optical constants of the V_2O_5 coatings. Further, the report on optical constants is yet not attempted in particular for thicker V_2O_5

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Table 1
Literature status on optical properties of V_2O_5 film/coating (*Pertinent information not provided in literature; IDG: Indirect Band Gap; DG:Direct Band Gap; DFG:Direct Forbidden Band Gap; S:Smooth; A:Amorphous; C:Crystalline; Q: Quartz and G: Glass).

Deposition Technique	Substrate	Phase	Thickness (nm)	Surface Roughness (nm)	Transmittance (%)	Detail of Optical Band Gap		Refractive Index	Extinction Coefficient	References
						Type of band gap	eV			
Sputtering	Q	A	21–243	*	90–70	DFG	2.14	*	*	[2]
Ion beam sputtering	*	*	100	*	90	*	2.24	*	*	[5]
Sputtering	Q	A	50	1.7	*	DFG	2.14	*	*	[6]
Electron beam evaporation	*	C	600	*	88	DFG	2.32	*	*	[7]
Sputtering	G	C	1000	*	90	IDG	2.25	2.53 (at 600 nm)	*	[8]
Sol–gel	G	C	*	*	85	DFG	3	2 (at 600 nm)	*	[9]
Sol–gel	G	C	*	*	*	DG or DFG	2.49	*	*	[10]
Sputtering	G	C	*	S	70	DG	2.59	1.85 (at 600 nm)	0.03 (at 600 nm)	[11]
Sol–gel	Q	A	145–210	*	75	*	*	2.31 (at 550 nm)	0.01 (at 550 nm)	[12]
Electron beam evaporation	G	C	600	*	60	DFG	2.3	2.1 (at 500 nm)	0.02 (at 500 nm)	[13]
Sol–gel	G	C	700	*	55	DG	2.3	*	*	[14]
Evaporation	G	A	309	8	70	DG	2.5	*	*	[15]
Spray pyrolysis	G	A	150	*	90	DG	2.34	2.4 (at 600 nm)	0.2 (at 600 nm)	[16]
Spray pyrolysis	G	A	*	*	80	DG	2.5	2.1 (at 900 nm)	0.2 (at 900 nm)	[17]
Pulsed laser deposition	*	*	*	*	75	DFG	2.47	*	*	[18]
Thermal evaporation	G	A	62	S	75	1st derivative	2.9	*	*	[19]
Evaporation	G	A	110	*	70	IDG	2.2	*	*	[20]
Thermal evaporation	G	A	181	*	80	IDG	2.2	2 (at 600 nm)	*	[21]
Atomic layer deposition	G	C	35	*	*	*	2.7	2.2 (at 600 nm)	0.2 (at 600 nm)	[22]
Sol–gel	Q	C	100	*	*	DG	2.8	2.1	*	[23]

coating though the same is used in thermistors for spacecraft application [24]. Therefore, in the present work thick V_2O_5 coating is grown on quartz and Si(111) substrates by pulsed RF magnetron sputtering technique. Further, optical properties such as transmittance and reflectance and optical constants such as optical band gaps, refractive index and extinction coefficient of deposited V_2O_5 coatings are evaluated.

2. Material and methods

A horizontally architectured pulsed RF magnetron sputtering system (SD20, Scientific Vacuum Systems, UK) was utilized to deposit V_2O_5 coatings on quartz and Si(111) substrates. The deposition was carried out at constant RF power of 700 W in room temperature. The deposition chamber was evacuated to a pressure of 5×10^{-6} mbar prior to coat and the working pressure was set as constant 1.5×10^{-2} mbar by introducing ultra high pure argon gas (~99.9998%, Praxair, India). Pure V_2O_5 (99.999%, Vin Korola, USA) target of 8 in. diameter was used. The thickness of the V_2O_5 target was 3 mm and it was bonded firmly with a 3 mm Cu backup. The duty cycle was kept constant as 57% and pulsing was done with 100 Hz.

Thickness of the coatings were measured using a nanoprofilometer (Nanomap 500 LS 3D, USA). The phase analysis of the coating was investigated by the X-ray diffraction (XRD) technique using a commercial diffractometer (X'pert Pro, Philips, The Netherlands). The $CuK_{\alpha 1}$ radiation was used at a glancing incident angle of 2° with a very slow step size of 0.03°. The microstructural characterizations were carried out by field emission scanning electron microscopy (FESEM: Supra VP 40 Carl Zeiss, Germany). The energy dispersive X-ray (EDX: X-Max, USA) spectra of the deposited film was acquired utilizing a customary unit (Oxford Instruments, UK) attached to the FESEM. The morphology and surface roughness and of the films were investigated using atomic force microscopy (AFM: CSEM, USA).

The transmittance and reflectance of the deposited coatings were measured by the UV–VIS–NIR spectrophotometer (Cary 5000, Agilent Technologies, USA) in the solar region (i.e. 200 nm to 2300 nm) of the spectral window. Further, the absorption coefficient (α) of the V_2O_5 coating was calculated from the experimental transmittance spectra using the following relation (1) [2, 10, 25]

$$\alpha = A(E_i - E_0)^a / h\upsilon \quad (1)$$

where, A is the comparative constant, E_0 is the initial photon energy, E_i is the incident photon energy, ν is the frequency and h is the Planck's constant. The magnitude of 'a' determines the type of electronic transition causing the absorption and can acquire values such as 3/2 for direct forbidden transitions. Tauc extrapolation [26] method was utilized to evaluate the optical band gap of the deposited films with $\alpha^{2/3}$ vs. photon energy (eV) plot. Envelope method was used to determine the dependency of refractive index (n) of the coating on wavelength from the reflectance spectra [15]. Extinction coefficient (k) was evaluated employing the conventional relation e.g., $k=\alpha\lambda/4\pi$ reported in literature [28]. Further, the thickness (t) of the deposited coatings can be theoretically calculated using the following relation (2) [18, 19, 28]:

$$t = (\lambda_1 . \lambda_2) / 2n(\lambda_2 - \lambda_1) \quad (2)$$

Where, λ_1 and λ_2 are the wavelengths corresponding to the two successive maxima or minima in reflectance spectra.

3. Result and discussion

Typical XRD pattern of deposited thicker (~4403 nm) coating