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Development of rf plasma sputtered Al_2O_3–TiO_2 multilayer broad band antireflecting coatings and its correlation with plasma parameters

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ABSTRACT

$TiO_2/Al_2O_3/TiO_2/Al_2O_3$ multilayer structures were obtained at different oxygen:argon gas ratios of 20:80, 30:70, 50:50 and 60:40 sccm and constant rf power of 200 W using reactive magnetron sputtering. Grain size and elemental distribution in the films were studied from AFM image and XPS spectra respectively. The deposited grain size increased with increasing oxygen:argon gas ratio. The optical band gap, refractive index, extinction coefficient were calculated from UV–vis transmittance and reflectance spectra. It was observed that the value of refractive index, extinction coefficient and band gap increased with increasing oxygen. These variations are due to the defects levels generated by the heterostructure and explained by the PL spectrum. The antireflecting (AR) efficiency of the films was estimated from the reflectance spectra of the films. Broad band antireflecting coating for the visible range was achieved by varying oxygen content in the film. The plasma chemistry controlled the antireflecting property by the interface interdiffusion of atoms during layer transition in multilayer deposition. The in situ investigation of the plasma chemistry was performed using optical emission spectroscopy. The plasma parameters were estimated and correlated with the characteristics of the films.

1. Introduction

In advanced technology, transparent, nano structured and multilayer coatings popularly known as artificial super lattices are gaining importance due to their superior optical properties compared to single layer [1,2]. Proper combination of refractive indices and interface reflectance losses across the interfaces decides the optical response of a multilayer stack. Therefore, material selection and the interface effect play a major role for fabricating multilayer optical windows. Oxide materials like TiO_2, SiO_2, HfO_2, ZrO_2 and Al_2O_3, etc. are usually used for multilayer optical windows [2–4]. For antireflection (AR), alternating layers of high and low refractive index materials are used which either lowers the overall intensity of the light or restrict the wavelength range of the light due to interference effect. There are many reports on the preparation of such optical coatings based on TiO_2/SiO_2 and Al_2O_3/SiO_2 multilayer dielectric films but less intensive reports are available on the combination of TiO_2/Al_2O_3 deposited by reactive magnetron sputtering [5–7]. TiO_2 has wide band gap (3.2 eV) [1–7] along with high refractive index (2.4), whereas, Al_2O_3 also has wide band gap (8.2 eV) but low refractive index (1.65). However, both these materials transmit visible light (600–800 nm) but absorb UV light (200–300 nm) [8,9]. Moreover, bulk TiO_2 and Al_2O_3 have no common lattice structure at any temperature or pressure [10]. There is a strong affinity for Ti–O–Al bond formation across a TiO_2–Al_2O_3 interface. This can avoid alteration of fundamental optical absorption edge (FOAE) [11]. According to Tikhonravov "maximum principle" theory, two stacks of greatest index contrast are sufficient to provide optimal optical performance at normal angles of incidence for any multistack film [11,12]. Therefore, two layers of TiO_2 and two layers of Al_2O_3 used alternatively to obtain four layer multilayer stacks for this study.

Plasma induced low temperature deposition like magnetron sputtering is the most conventional method for such depositions. The plasma chemistry involves large number of reactive species generated in the reaction zone which plays important role for the endpoint detection and process control. However, the major disadvantage in deposition process arises due to the target poisoning. The radiation from the generated species in the plasma gives a concrete signature of the plasma chemistry that can be correlated with the deposited materials characteristics. The optical emission spectroscopy is a powerful non-intrusive method to monitor the in situ deposition mechanism with respect to plasma radiation. This helps

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in deciding the optimal conditions for deposition of films of desired qualities.

In view of this, $TiO_2/Al_2O_3/TiO_2/Al_2O_3$ multilayer antireflecting (AR) coatings consisting of four layers which is popularly known as prime graded selective absorber coating (PGSAC) is reported here [13]. The present work aims to study the impact of oxygen:argon gas ratio at constant working pressure on the optical properties of the hetero structures. The interdiffusion mechanism and the intermixing of the two materials Ti and Al during deposition have been investigated using the non-intrusive optical emission spectroscopy.

2. Experimental details

Heterostructures of $TiO_2/Al_2O_3/TiO_2/Al_2O_3$ thin films were prepared using rf magnetron sputtering deposition system (MSC-3, JE Plasma Consult GmbH). The details of the deposition system have been given in our earlier communication [14]. The oxygen:argon gas flow rate was maintained at 20:80, 30:70, 50:50 and 60:40 sccm with the help of mass flow controller at constant rf power of 200 W for deposition. The deposition was performed at working pressure of $\sim 6.2 \times 10^{-2}$ mbar. The deposition was for 20 min for each layer without breaking the vacuum and switching on from one magnetron to other at transition. In this way, four equal thick films (~400 nm) are obtained at different oxygen:argon gas ratio, but constant rf power and deposition time of 20 min each layer.

The optical emission spectroscopy (getSpec UV/Vis 0172 grating UA, 200–720 nm, CCD detector with 3648 pixels, 10 μm entrance slit and spectral resolution of 0.27 nm) has been used for in situ investigation of the plasma chemistry showing the intermixing of the two metals during interface formation of the heterostructure. The chemical state and composition of the films were checked through X-ray photoelectron spectroscopy (XPS) measurements (Perkin Elmer PHI ESCA 5500 system). The surface morphology and the particles size was determined using atomic force microscope (NT-MDT Moscow, Russia, Model No. Solver P47-PRO). The film thickness and the optical characteristics of the deposited films were examined using an ex situ Ellipsometer (Nano-View Inc., Korea; SEMG1000-VIS) and by UV–vis and PL spectrophotometer (Perkin Elmer). The AR performance of Al_2O_3 and TiO_2 four layer stacks on glass deposited at optimal growth conditions were studied using a UV–vis spectrophotometer (Perkin Elmer).

3. Results and discussion

3.1. Study of gas phase deposition using optical emission spectroscopy (OES)

Fig. 1 shows the typical line of sight space integrated optical emission spectra of plasma during successive deposition of four layers of TiO_2 and Al_2O_3 heterostructure at oxygen:argon 20:80 sccm. The spectrum presents the characteristic emission lines of Ti (393.42, 428.49, 474.27 and 564.85 nm), Al (396.15 and 669.6 nm), Ar (603.21, 688.81, 696.54, 714.7 and 726.51 nm) and O (645.41 nm). Table 1 gives the detailed transitions of the observed emission lines. However, the emission lines from the reactive gas (OI) typically are quite weak and difficult to detect with respect to the metal lines [15]. The intensity of the metal peaks decrease as the partial pressure of the reactive gas increases. The Al lines (396.15 and 669.6 nm) seems to be absent during deposition of 1st layer, however, for all the other successive layers, the spectral lines of Ti, Al and Ar were detected. The plasma becomes more contaminated with metal species as the successive layers get deposited from 1 to 4 without breaking the vacuum and disturbing the ambience. The presence of the emission lines corresponding to both Ti and Al clearly reveal the real-time evidence of the intermixing of the two

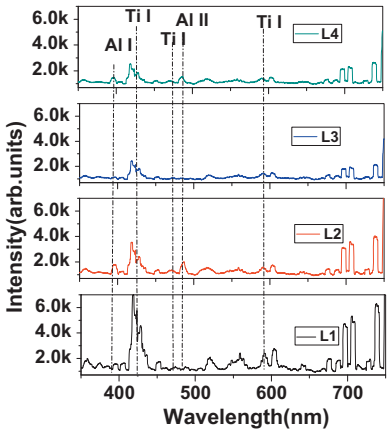

Fig. 1. Layer wise emission spectra during deposition at 20:80 sccm oxygen:argon gas ratio.

Table 1
Studied emission lines with the corresponding transition, the emitted wavelengths and their upper level energies.

Species	Transition system	Upper level energy (eV)	Emitted wavelength (nm)
Ti I	$a^3F–y^5D^0$	3.19	393.42
Ti I	$a^5P–y^5S^0$	4.63	428.49
Ti I	$a^3H–x^3H^0$	4.84	474.27
Ti I	$z^3D^0–e^3F$	4.68	564.85
Al I	$^2P^0–^2S$	3.14	396.15
Al I	$^2S–^2P^0$	4.99	669.60
Ar I	$^2[5/2]–^2[7/2]^0$	15.13	603.21
Ar I	$^2[3/2]–^2[3/2]^0$	14.97	688.81
Ar I	$^2[3/2]^0–^2[1/2]$	13.32	696.54
Ar I	$^2[3/2]^0–^2[3/2]$	13.28	714.70
Ar I	$^2[3/2]^0–^2[3/2]^0$	14.85	726.51
O I	$^5P–^5S^0$	12.66	645.44

metals during interface formation at the time of transition from one layer to other. This helps us to understand the growth mechanism as well as determine the possible electron temperature during the growth. Reactive magnetron sputtering deposition involves low pressure, low temperature plasmas under partial local thermodynamic equilibrium (PLTE). The Ar line intensities of 603.29 and 714.7 nm have been used for determining the electron temperature using relative intensity method given by [16].

$$T_e = \frac{E_m - E_p}{k \ln(I_{pn} A_{ms} g_m \nu_{ms} / I_{ms} A_{pn} g_p \nu_{pn})} \quad (1)$$

where I_{ms} and I_{pn} are the measured intensities from m–s and p–n transitions, respectively, A_{ms} and A_{pn} the transitions probabilities, ν_{ms} and ν_{pn} wave numbers, E_m and E_p are the upper level energies, g_m and g_p their statistical weights and, k the Boltzmann constant. In order to minimize the error in the calculation of the electron temperature, the difference between energy levels should be large and wavelengths of selected lines should be neighbouring [16]. The different parameters of the Ar lines used for T_e calculation are taken from NIST database and presented in Table 2 [17]. However, the assumption of partial local thermo dynamic equilibrium is not likely to be satisfied, and so, the calculated T_e value is questionable [18].

Table 2
Parameters used to calculate T_e from Eq. (1).

λ (nm)	E (eV)	g	A (S^{-1})
603.29	15.13	9	2.46×10^6
714.70	13.28	3	6.25×10^5