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Improving the stoichiometry of RF-sputtered amorphous alumina thin films by thermal annealing

High quality alumina thin films were deposited on glass substrate by reactive radio-frequency sputtering. The deposition process and rate were controlled by radio-frequency power and reactive gas (oxygen) flow rate. The relationships between O/Al ratio contents and the structural, electrical resistivity and optical parameters of the films were investigated. The O/Al of the films varied with change in oxygen flow ratio, power density and post deposition annealing. The structure and phase of the films were unaltered as the deposition parameters and post deposition annealing up to 573 K were varied. O/Al of 1.5 was obtained at oxygen flow ratio of 11%, radio-frequency power of 250 W and post deposition annealing of 573 K. The sheet resistance of the films were all very high but the same within experimental uncertainties. The optical parameters (transmittance, refractive index and extinction coefficient) of the films varied considerably and depended on the films' stoichiometry.

Keywords: Alumina; Thin films; Amorphous; Stoichiometry; Optical constants

1. Introduction

Alumina thin films can be obtained in amorphous and different crystalline phases [1–3]. The high temperature requirement for the formation of the crystalline phases [4–8] has limited their deposition on temperature-sensitive surfaces. Subsequently, due to their low temperature requirement, amorphous alumina has become the most common form [1] and can be deposited on a variety of substrates for different applications depending on which of its properties is being explored.

Many properties of amorphous aluminium oxide including high optical transparency [9], chemical and thermal stability [10, 11] have led to the successful applications of alumina films in optical, electronics and protective coatings [12–15]. How successful the films are in these applications depends on their homogeneity and chemical inertness. The two factors which depend on films' deposition method and parameters are serious challenges in film deposition.

Aluminium oxide films in recent times have been successfully deposited using different methods [9, 16–32]

with interest in their diverse properties and applications. Few of these works however have investigated the optical properties of amorphous alumina films, and fewer have paid attention to how stoichiometry affects the optical behaviour. Alumina is the only stable oxide of aluminium (Al) [33], and thus in the absence of an atom of any other element, a chemical combination of Al and oxygen (O) would always give alumina (which may be amorphous or any of the known crystal phases depending on temperature of formation [1–9]). Although, non-stoichiometry of alumina film could be deliberate and desirable in some applications [34–38], it should however be noted that excess of either Al or O (non-stoichiometry) in Al_2O_3 constitutes an impurity and can impact on the films' properties. Therefore, the use of optical characterization of alumina films, as it used to be the case, for validation of deposition method may not be adequate. This is because optical behaviour may not necessarily indicate good stoichiometry [16, 17]. Thus a comparison of optical properties of alumina films deposited by different methods will require that the stoichiometry of the films from the methods is the same. Therefore, there is the need to understand the relationship between stoichiometry and optical behaviour of aluminium oxide.

Reactive radio-frequency (RF) sputtering is a commonly used deposition procedure for compound films where good controls of thickness are required. RF sputtering has been used [17, 39–43] for the deposition of aluminium oxide films in many studies without much emphasis on stoichiometry and its relation to optical properties. This may be due to the fact that an appreciable number of parameters are available for permutation to achieve stoichiometry. These parameters, which affect the deposition rate and film composition in different ways, include RF power density, sputtering and reactive gas flow ratios with partial pressures, base and total pressures. Many efforts at depositing stoichiometric alumina film by RF sputtering [17, 39–43] with minimal parametric variation have rarely succeeded.

In this research, stoichiometric amorphous alumina films were deposited by a sequential variation of just three parameters – oxygen flow ratio, RF power and post deposition annealing temperature. The effects of these parameters on deposition process, film composition and film optical parameters were also investigated.

2. Experimental procedure

Aluminium oxide films were deposited on clean 1.20 mm thick 25 mm × 76 mm glass (microscope slides) substrates in an RF (13.56 MHz) sputtering unit (Edwards Auto306). Al (99.99%) of 10 cm diameter was used as the target with argon (99.99%) and oxygen (99.99%) gases as the sputtering and reactive gas respectively. To investigate the influence of deposition parameters on films' composition, both the RF power and the oxygen flow rate were varied while the argon flow rate was kept constant at 1.0 sccm. Both the sputter and reactive gases flow rates were controlled by mass flow controllers. The different sets of deposition parameters used for the different films are given in Table 1. Prior to each deposition, the sputtering chamber was pumped down via a turbo molecular pump to a base pressure 10^{-5} Torr. The depositions were done at different working pressures as dictated by the total gas flow rates. All the films were 50 nm thick with the films' thicknesses set electronically on the control panel of the sputtering unit. Some of the films were annealed after deposition in ambient air for two hours at 473 K and 573 K.

The films' structural/phase characterisation was done using a (PAnalytical X'pert Pro MPD) X-ray diffraction (XRD) unit with Cu-K $_{\alpha}$ ($\lambda = 1.54 \text{ \AA}$) radiation. The primary beam divergence was sufficiently small to allow for the required resolution of low glancing angle of incidence. XRD at grazing incidence was used to avoid the contribution related to the glass substrate. The instrument was operated in a step scan mode in increments of 0.004 and counts were accumulated for 1.91 s at each step. Sheet resistivity of the films was measured by the four point probe method. The films elemental composition was studied using Rutherford backscattering spectrometry (RBS) using 2 μC of 2.2 MeV $^4\text{He}^+$ beam from the ion beam analysis facility at the Centre for Energy Research and Development, (O.A.U) Ile-Ife, Nigeria. This facility is centred on an NEC 5SDH 1.7 MV Pelletron Accelerator, equipped with an RF charge exchange ion source. The ion source is equipped to provide proton and helium ions. A quantitative analysis of the RBS spectra was made using the computer code SIMNRA [44]. The analysis comprises of simulating each spectrum in comparison with the experimental one.

For optical characterisation, optical transmission and reflectance spectra were acquired for photon wavelengths between 200 nm and 1100 nm using a UV-VIS spectrophotometer (Thermo Scientific Helios Omega).

Table 1. Deposition parameters of the films.

Film ID	Oxygen Flow Ratio (%)	RF Power (W)	Annealing Temperature (K)
A	11	200	–
B	18	200	–
C	27	200	–
D	11	200	473
E	11	200	573
F	11	150	573
G	11	300	573

Optical constants (i.e. refractive index (n) and extinction coefficient (k)) are two parameters which characterise how a material interacts with electromagnetic radiation. In this study, the refractive index, and the extinction coefficient, of the films were calculated from measured reflectance and transmittance data according to the equations [45]:

$$n(\lambda) = \frac{1 + \sqrt{R(\lambda)}}{1 - \sqrt{R(\lambda)}} \quad (1)$$

$$k(\lambda) = \frac{\alpha(\lambda)\lambda}{4\pi} \quad (2)$$

$$\alpha(\lambda) = \frac{\ln\left(\frac{1}{T}\right)}{d} \quad (3)$$

3. Results and discussion

3.1. Influence of deposition parameters on rate of deposition

Ar:O flow ratios between 11% and 27% yielded quality films. Increasing the flow ratio beyond 27% drastically reduced the deposition rate and caused high pressure build up in the chamber which eventually shut down the sputtering system. Oxygen flow ratio less than 11% yielded brown films, a possible indication that the aluminium was not fully oxidised. The 11% minimum is in agreement with a suggestion of a flow ratio in excess of 8% for formation of alumina film [17]. Increasing the flow rate from 11% to 27% reduces the deposition rate as shown in Fig. 1. The decrease in the deposition rate can be attributed to any or all of the following reasons [43]:

- Higher oxygen flow rate results in more oxygen gas molecules in the deposition chamber and consequently leading to increase in oxygen partial pressure and total gas pressure within the chamber. Due to this high pressure, sputtered Al atoms collide with more atoms thereby losing energy and subsequently slowed down their arrival to the substrate.

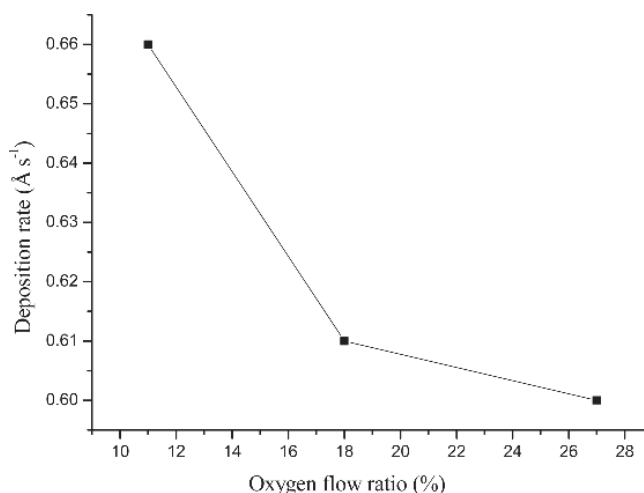


Fig. 1. Variation of deposition rate with oxygen flow ratio.

- Availability of excess oxygen gas within the chamber could cause the formation of Al_2O_3 layer on the surface of the target (target poisoning). Since the sputtering yield of alumina is less than that of Al, this ultimately results in fewer sputtered atoms (sputtering rate) and consequently the deposition rate is reduced. This is the major reason for the decrease in deposition rate because excess oxygen reacts with the target first before contributing to pressure build up in the chamber.

Increasing the RF power from 150 W to 250 W was observed to increase the deposition rate of the film in an almost linear manner (Fig. 2). This increase is due to increase in sputtering yield of the target brought about by the RF power density increase.

3.2. Structure and sheet resistance of deposited films

The XRD spectra at different oxygen flow ratios, RF powers and annealing temperatures are presented in Fig. 3. Apparently, there is no significant difference between the films' spectra and this suggests a consistence of phase. Furthermore, the absence of prominent peaks in the XRD patterns of the films suggests that they are predominantly amorphous. This is consistent with the fact that amorphous alumina is formed at temperatures below 673 K irrespective of deposition method and doping [4, 9, 31, 46, 47]. Amorphous alumina has been attributed to the presence of AlO_5 , which is responsible for the disorder and also hinders the

growth of crystalline alumina phase [4]. Although, amorphous alumina contains both AlO_4 and AlO_5 coordination in the ratio 2:1 [4, 48, 49], AlO_5 is transformed to AlO_4 and AlO_6 coordination at high temperature (>1073 K) in different proportions in the different crystallographic polymorphs of alumina depending on the temperature of transformation [4, 48–50].

As shown in Table 2, the films exhibited high sheet resistance, an indication that they are insulators. The change in

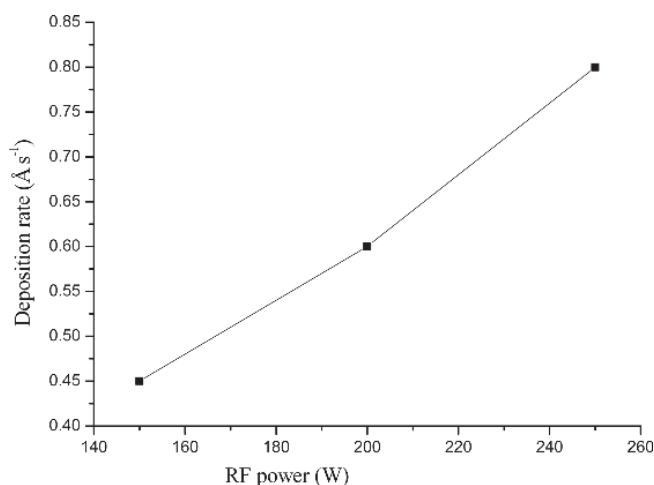


Fig. 2. Variation of deposition rate with RF power.

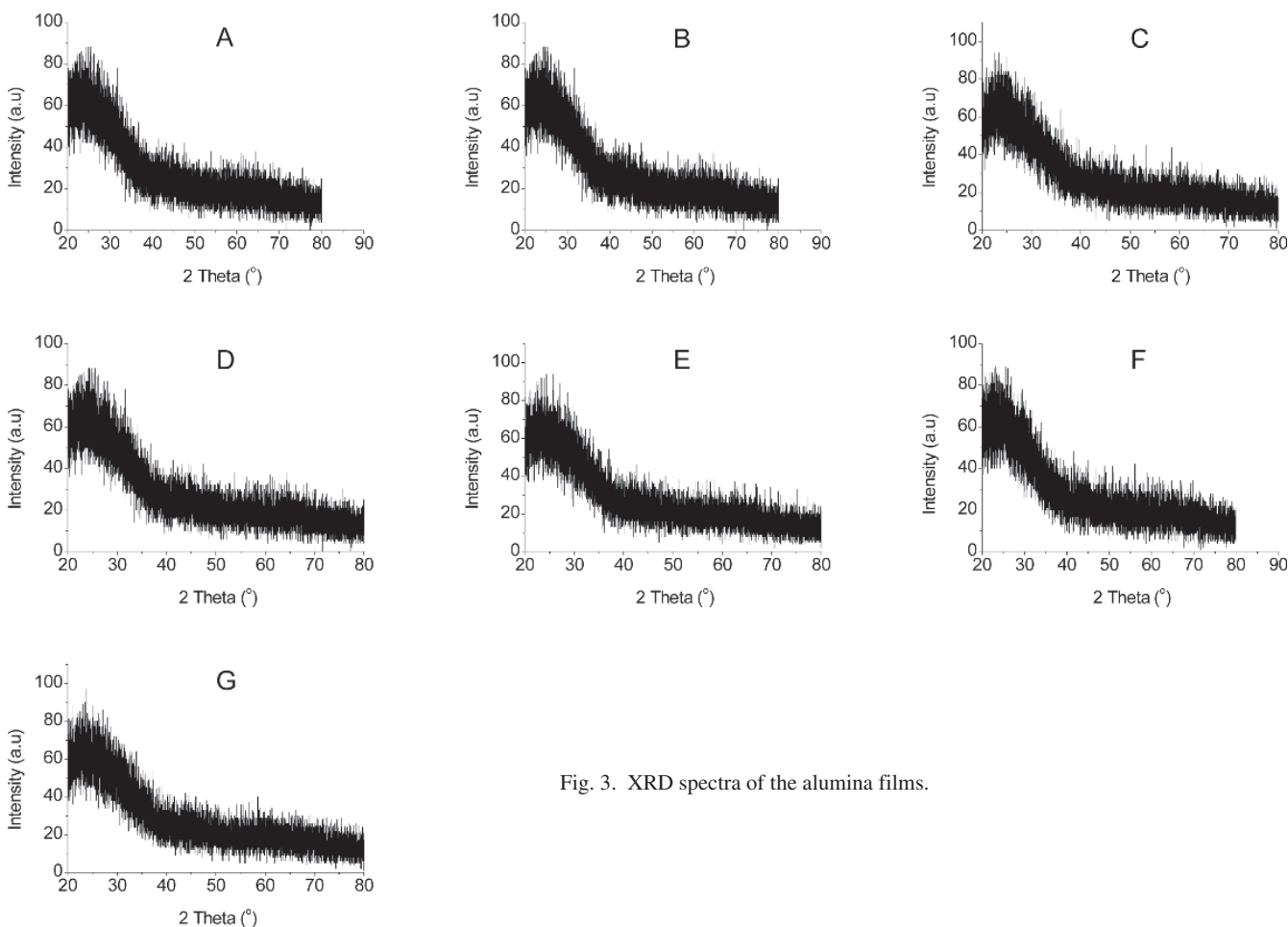


Fig. 3. XRD spectra of the alumina films.

Table 2. O/Al ratio, and sheet resistance of the films.

Film ID	RBS Analysis (O/Al)	Sheet Resistance (Ω square) $\times 10^8$
A	1.92	2.71
B	2.51	2.75
C	2.60	2.73
D	1.69	2.78
E	1.55	2.73
F	2.06	2.72
G	1.50	2.69

sheet resistance of all the films did not show any regular pattern with oxygen flow rate, RF power and annealing temperature.

3.3. Film stoichiometry

3.3.1. Influence of oxygen flow ratio on stoichiometry of Al_xO_y

The variation in stoichiometry of as deposited Al_xO_y thin films (A, B, and C) with oxygen flow ratio at RF power of 200 W is presented in Table 2. The table shows a general linear increase in O/Al ratio in the deposited films as the O flow rate increases. Although none of the films (A, B, C) gave the required O/Al ratio (1.5), the increase in the O flow made the film oxygen rich. The increase in O/Al ratio as oxygen flow rate increases does not imply that the number of sputtered Al atoms is reducing but simply due to one or all of following reasons. Firstly, the O atoms introduced into the chamber react with sputtered Al atoms on the substrate and at the sputtering chamber wall. Increasing the flow rate of oxygen gas beyond the critical value of 8% [17] could cause excess O atoms to react with the Al target thus causing a thin layer of alumina to be formed on the target surface [41]. Although the energy transfer factors of O (1.0) and alumina (0.935) [51] are almost equal, the possibility of preferential sputtering of O from the alumina formed at the surface of the target exist but very low. Thus Al–O and perhaps O atoms are sputtered rather than Al atoms [39]. Hence the number of O atoms at the substrate becomes relatively higher than the concentration of Al at the substrate. Secondly, an increase in the oxygen content in the sputtering chamber diminishes a relative Ar (flux) ion concentration. This brings about a corresponding increase in the plasma (working pressure within the chamber). The result of this is the reduction in the mean free path of the sputtered Al atoms and an increase in the number of collisions with neutral atoms per path length and corresponding loss in energy. Few Al atoms would therefore have sufficient energy to overcome the activation energy barrier to react with oxygen atoms [43]. Finally, an increase in oxygen flow marks an increase in O flux and energy impacting the substrate surface, leading to adsorbed O species at the surface of the film [52].

All the mentioned factors could have contributed to the observed decrease in aluminium content of the films (Table 1) and also suggest that one sure way of controlling the chemical composition of RF sputtered alumina and im-

prove its stoichiometry is to control the reactive gas (O) entering the sputtering chamber.

3.3.2. Influence of annealing temperature on stoichiometry of Al_xO_y

It is worthy of note that the transformation of aluminium to alumina is not a continuum with oxygen content but rather a change across a thin range of compositions [17, 41, 53, 54]. This is due to the fact that Al_2O_3 is the only stable oxide of the Al–O system. Consequently it is expected that the excess oxygen atoms remain as volatile species in the films. These impurity atoms in the alumina films are mobile and can create an illusion of a smooth film surface. Also the free oxygen atoms can react easily with other radicals in the films' environment to give more complex impurities in the films. Thus, it is a necessity that such excess oxygen be removed when stoichiometric alumina is required. Post deposition heat treatment has been found to increase the adhesion of alumina films to substrate by eliminating trapped excess vacancies irrespective of deposition method [55]. To this end, the film with the lowest O/Al content ("A" in Table 1) was annealed at two different temperatures (473 K and 573 K). The annealing temperature was limited to 573 K due to the fact that higher temperature could cause uneven expansion of the substrate/film combination and or cause phase conversion among the metastable forms of alumina possibly leading to cracking/fracture of the film's surface [40]. More so, higher temperature could lead to deterioration of the glass substrate and since the surface of alumina is active at higher temperature [56], diffusion of substrate elements or from the film's environment is highly likely [16]. The O/Al ratios of the annealed films ("D" and "E") compared with as deposited film ("A") from RBS analysis showed a decrease in the O content of the film as temperature is raised. The improvement towards stoichiometry of alumina films simply means that the temperature increase caused an evaporation of volatile oxygen from the films. The implication of this is that post deposition heat treatment or high substrate temperature could improve stoichiometry of thin alumina films.

3.3.3. Effect of RF power on stoichiometry of Al_xO_y films

In the reactive RF magnetron sputtering of alumina, one can increase the number of sputtered Al atoms that reach the substrate by: reducing the time of flight of Al atoms, increasing its mean free path, and increasing the aluminium ion current. All of these can be achieved by increasing the RF power of the sputtering system [57]. Since the number of sputtered aluminium atoms that reach the substrate can be controlled by the RF power, alumina was deposited at an oxygen flow ratio of 11% at RF powers of 150, 200 and 250 W with post deposition annealing at 573 K. It was observed that the increasing RF power density decreased the relative concentration of O in the films ("E", "F" and "G"). The decrease was because of the increase in the Al ion density in the plasma and thus increasing the aluminium concentration in the films. The annealing of the films at 573 K compliments the reduction in the relative oxygen content of the film by increase in power. The increase in power density can thus improve the stoichiometry of RF

sputtered aluminium oxide from an aluminium target. The film sputtered at RF power of 250 W with oxygen flow ratio of 11 % and annealed at 573 K after deposition gave stoichiometric alumina for the sputtering system used in this research. Generally, the obtained O/Al ratios (1.50–2.60) in this work are within earlier reported values [39, 52, 58]. The obtained stoichiometry (O/Al) of 1.69 (“D”), 1.55 (“E”) and 1.50 (“G”) are all within the reported range of stoichiometry alumina on glass [59, 60] and are comparable to those obtained using similar deposition technique: 1.54–1.78 [17]; 1.49–1.93 [36]. However, a careful combination of O flow ratio, RF power and annealing temperature was able to give good stoichiometry (1.50).

3.4. Optical parameters and stoichiometry

Physical observation of the films showed that they are transparent and colourless. The optical transmittance (T) spectra of the deposited alumina films on glass are presented in Fig. 4a and b. T was recorded using uncoated glass substrate as a reference. The small undulations noticed on the spectra (Fig. 4b) are due to interference patterns. The transmittances of all the films showed a similar pattern in their variation with photon wavelength. In the region be-

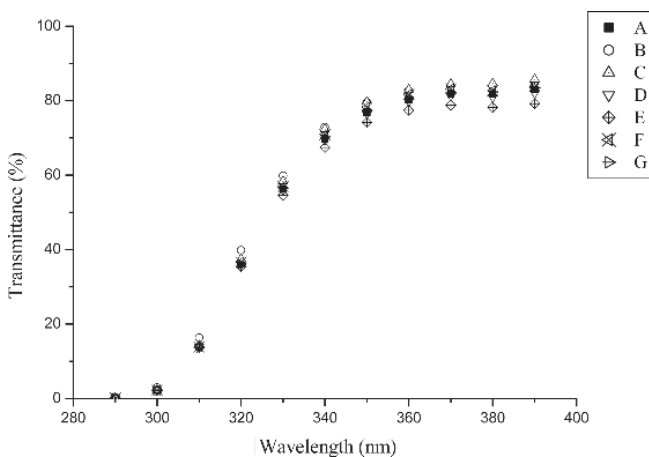


Fig. 4a. Transmittance spectra of the films in the UV region.

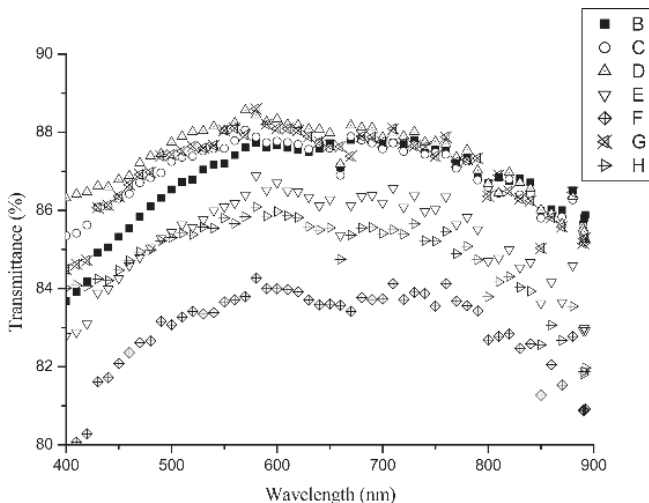


Fig. 4b. Transmittance spectra of the films in the VIS-IR region.

tween 200 nm and 300 nm (Fig. 4a), T is very low and less than 20 % but rises steadily from 300 nm. There is no noticeable difference between the T of the films (variation within just 2 %) in this region irrespective of the oxygen flow ratio and annealing temperature. In the VIS-IR region (400–1100 nm), the films were all transparent with T greater than 80 % (Fig. 4b). T is higher for oxygen rich films except for sample E (O/Al = 1.55). Hence, T of films increases linearly with O content in excess of 1.55 in the VIS-IR region. The differences in T for the films are all within 10 % irrespective of the excess O level. The differences in T for all the films can be attributed to the differences in their O/Al ratio which was brought about by differences in deposition parameters. The difference in the transmittance can be physically attributed to change in density/porosity induced by variation in oxygen content.

As shown in Fig. 5, the variations in the evaluated n and k at 550 nm with oxygen content were similar. This implies that the absorption and reflection of photons by the film is not the same. Both n and k initially increased and then decreased when the oxygen flow rate was increased (samples A, B, and C). Whereas both n and k decreased as the temperature of annealing was increased (samples: A, D, and E). However, there was no clear correlation between RF power and n and k values. Overall n and k varied inversely with optical transmittance. The range of refractive indices of the alumina films obtained (1.66–1.83) was in good agreement with values reported (1.65–1.85) in earlier studies [4, 61–65].

4. Conclusions

The structure (phase), electrical resistivity and optical properties of RF sputtered alumina film on glass at different deposition parameters were investigated. Film prepared at various oxygen flow ratio, RF power and annealing temperature up to 573 K exhibited predominantly amorphous structure with high sheet resistivity. The oxygen content of the films varied with the three deposition parameters considered, increasing for increasing oxygen flow rate, but decreasing as either annealing temperature or power density was increased. The optical transmittance also changes with high consistency with the oxygen content of the film. The variation of optical parameters with deposition parameters

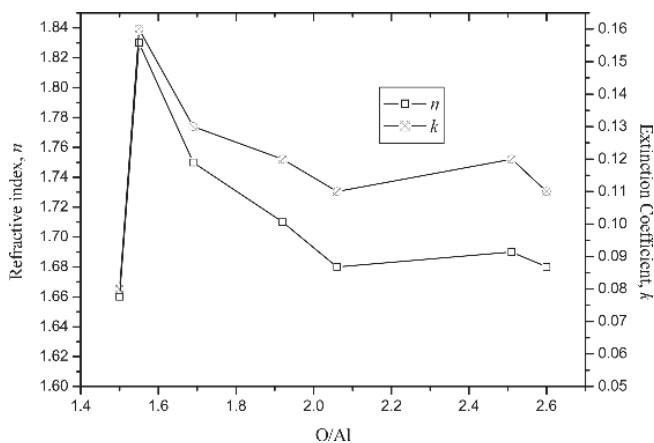


Fig. 5. Variation of n and k with stoichiometry at a wavelength of 550 nm.

and post deposition annealing suggests that a careful choice of these parameters can yield alumina of different oxygen content for various applications. Stoichiometric, dense and high refractive index alumina film was obtained at 11% oxygen flow ratio and RF power of 300 W and annealing temperature of 573 K.

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