CHAPTER IV

DISCUSSION

4.1 INTRODUCTION :

To the author's knowledge there are no reports available on porous Al_2O_3 thin films obtained by oxidation of Al in steam. Also not much work has been done on the adhesion of the porous Al_2O_3 thin film.

The results on steam oxidised Al_2O_3 thin films indicate that for moisture sensor applications, these films can be of great use, since the adhesion of these films are very much higher than porous Al_2O_3 films obtained by other methods. The porosity of these films are comparable with those of hot water oxidised films and anodic oxide films. This chapter attempts to give possible explanation to the various results reported in chapter III.

4.2 FORMATION OF POROUS ALUMINIUM OXIDE :

The aluminium oxide films studied are formed by the reaction of thin film of aluminium with water,the water being either in the form of hot water at 60°C or steam.The mechanism of growth of these oxide films have to be understood for the proper analysis of the properties like refractive index, adhesion and D.C. resistance.

Accoding to Vedder et al[79] the reaction between aluminium and water takes place according to the following steps.

i) Amorphous oxide formation on exposure of fresh aluminium to atomosphere.

ii) Dissolution of the amorphous oxide in water.

iii) Precipitation of aluminium hydroxide in to the aluminium oxide.

These processes are dynamic in nature. If thin films of aluminium is used, the thickness of hydroxide keeps on increasing resulting in complete conversion of aluminium to aluminium hydroxide. The rate determining step in the formation of hydrated oxide from the Al-water reaction is the hydration transitary anhydrous oxide. It has been reported[84] that the hydrated product consists of loosely connected platelets and is highly porous. The pores extend from top to bottom of the film and its hydroxyl ions are arranged along the pore walls.

Pore nucleation is also influenced by Al grain boundaries, surface inhomogenity and local heating[28,29]. Murphy and Michelson[90] have suggested that the oxide layer consists of colloidal particles which are free to rearrange under the influence of external forces. During oxidation of Al under steam, the higher temperature of steam might be changing the pore nucleation and rearrangement of the platelets.

4.3 STEAM OXIDISED AND HOT WATER OXIDISED Al_2O_3 THIN FILMS :

The rate of formation of Al_2O_3 by steam oxidation is higher than that formed due to hot water. It has been observed by Phatak et al[18] that at temperature $> 58°C$ the rate of growth increases unusually. Possible transformations occuring in situ which involve volume changes as a result of differences in bulk densities. Such transformations have been reported to occur above 70°C[91]. Evaporated aluminium films are known to be more active than bulk aluminium so possibilities of such transformations are more.

McDonald and Butler[27] have reported that below 150°C the hydrated oxide transforms into various forms $Al(OH)_3$, bayerite and gibbsite ($Al_2O_3 \cdot 3H_2O$), boehimite ($Al_2O_3 \cdot H_2O$) etc. An increase in the rate is also observed at 100°C[11]. Due to the temperature being higher during steam oxidation, the degree of crystallinity and composition of the initial oxide film may vary locally as compared to hot water oxidised films which could also affect the growth rate.

It is well known that variety of suboxides of Al are capable of existance, but all are unstable at room temperature.

The oxidised films are SEM insensitive as no structure could be obtained. The films are seen to be featureless. The XRD patterns (fig. 3.6.2(a) and fig.3.6.2(b)) of both the Al_2O_3 film indicate a poor degree of crystalinity. It has been reported that Al-water reaction above 80° C is α-Al_2O_3 H_2O. Our XRD data of steam oxidised Al_2O_3 films show a predominantly α-modifications of Boehimite. The formation of Al_2O_3 at 80° C has also been confirmed by electron diffraction pattern.[83]

There are no reports of porous Al_2O_3 having δ-Al_2O_3 form. Our hot water oxidised Al_2O_3 films show predominantely δ-phase of Al_2O_3. It has been observed by Lippens[92] different temperature products are obtained with Al-water reaction.

In the infra-red spectrum of both steam oxidised and hot water oxidised Al_2O_3 films a slight absorption is observed in the region 2500 cm^{-1}- 3800 cm^{-1}.G.A.Dorsey[34] has attributed this band to the presence of water, free adsorbed or as hydroxide. It has been also reported[79] that bands at 3280 cm^{-1} and 3090 cm^{-1} are due to pseudoboehimite. Pseudoboehimite contains more hydroxyl than corresponds to the formula AlOOH. Such excess hydroxyl give rise to a broad structure-less absorption band much like in the spectrum of entirely amorphous aluminium hydroxide.

Since the XRD results showed more amorphous arrangement, the possibility of pseudo-boehimite in α and δ

phases being formed. Other hydroxydes such as bayerite or boehimite always exists in well crystalline forms.

4.4 REFRACTIVE INDEX OF STEAM OXIDISED AND HOT WATER OXIDISED Al_2O_3 THIN FILMS :

The films studied are only upto ~ 1600 A°, where there is a thickness independent refractive index with a maximum limiting porosity of 38% for steam oxidised and 49%. for hot water oxidised films. Most of the porosity data reported in literature are of films greater than 2000 A°. A thickness independent refractive index is also reported by Jadhav et al[69] for hot water oxidised Al_2O_3 films upto 2000 A° thickness. The aluminium oxide molecules nucleates initially onto the substrate in platelets form [79] and few platelats join over small areas forming crystallite with substantial mismatched boundries causing distribution of porosity in the films. When the oxide nucleates onto hot substrate (70°C) for steam oxidised film there is a densification of platelets of the hydroxide. This densification may be causing decreased porosity and increased refractive index. Differences in porostiy have beeen observed by Alluit et al[6] for anodic film due to changes in temperature. When aluminium is under steam there is excess of oxygen present due to oxygen in the atmosphere. At around 70°C it has been reported[18] different forms of hydrated oxide states forming in Al_2O_3 which might also affect the refractie index and hence packing density and porosity.

The specific surface area of the loosely connected platelets is very high, typically several hundred m^2/gm.[30] These hydrated Al_2O_3 layers are very sensitive to the presence of water vapor in the ambient atmosphere. On exposure to moisture, water molecules are absorbed into these films and change of density take place. The water molecule tend to be adsorbed on the surface and/or condense at the pores. The refractive index of water is 1.33 which is less than that of the films. If water were to fill up the pores one would expect the refractive index to decrease. The decrease of refractive index of the hot water oxidised films are more than steam oxidised films, especially the films of lower thickness. It is expected that the porosity varying by only 2% between thinner and thicker films, the surface to volume ratio is lower at lower thickness. At higher thickness one expects more surface area so that more absorption of moisture can take place, resulting in more changes for higher thickness films. Such trend is shown slightly in steam oxidised films, but not by hot water oxidised films. The very process of preparation of hot water films by immersing in hot water (60°C) might be producing films with already partially filled pores especially for thicker films.

The sequential exposure effects (fig.3.3.3.2 table 3.3(c)) confirms the above, that the pores are already partially filled with moisture. Since the decrease in refractive index observed is greater than that obtained with only moisture exposure. On heating to 40°C all the water in pores might desorb and the film become a mixture of hydroxide and air which has lesser refractive index than hydroxide + water, since the refractive index of air is 1.00 compared to 1.33 i.e. refractive index of water.

The increase in refractive index on exposure to moisture is due to the pore filled with water,where lesser humidity percentage giving lesser changes. The repeated decrease and increase in refractive index on repeating the sequence indicate a adsorption desorption type of process responsible for thr refractive index change.

On heating to 120°C the refractive index changes are considrably higher than heating to 40°C indicating simple process no longer dominate the properties of the films. Al_2O_3 is known to absorb water as undissociated molecules, bonded to the underlying surface. Peri and Hannan[93] using infra-red have shown that at low temperature undissociated water molecules are present above 100°C, the water not only desorbed and removed from system, but also reacts to form surface hydroxyl group both inside the pore walls and also on the film surface. The reason why steam oxidised films change more on heating to 120°C is not clearly understood.

4.5 ADHESION :

From fig.3.4.1 it is seen that the adhesion of steam oxidised films is higher (~ 430 KgF/cm^2) than hot water oxidised films (~ 300 KgF/cm^2). The increase in adhesion is sufficiently higher than the error limit ± 9.8KgF/cm^2. Inspite of being porous these films show quite high adhesion. These films are formed by oxidation of aluminium films deposited by vacuum evaporation. Aluminium being an oxygen active metal and also having a strong gettering effect for oxygen suggest a strong bonding with the substrate due to interfacial oxide layer. The adhesion of aluminium film[94] is around 275 KgF/cm^2. Al also has a high value of heat of oxide formation[95], where by interfacial oxide layer formation takes place immediately. The aqueous oxidation process of conversion of thin films of Al to Al_2O_3, slightly increases the adhesion as compared to Al only. Where as in the steam oxidation process the effect of the substrate getting hot (~ 70°C) during the passage of steam might be enhancing the chemical bonding interface layer due to increase in mobility, at the interface. The fact that packing density (Art.3.3.2) is higher for steam oxidised films, indicates higher adhesion of these films as compared to hot water oxidised films. The range of adhesion values obtained for these films are comparable to those obtained by electron beam evaporation of Al_2O_3.[96] The porous films having such high adhesion is indeed surprising. ESCA analysis at the interface has to be done to find the nature of interfacial bonding.

On exposure to moisture the water molecule tend to act as impurity atom reacting with the host lattice or form solid phase, separate from the host phase. This produces additional stress in the films. Also high stress are often introduced, because of volumetric changes involved in forming new phases[97]. Hirsh[98] has reported that adsorption of polar molecules like water in porous films causes substential tensile stress, through mutual electrostatic repulsion of the adsorbed molecules dipole. This results in an increase in intrinsic stress resulting in decrease in adhesion. It is felt that Al_2O_3 obtained by oxidation of Al by steam, produces films with lesser defects at the interfacial layer due to which the changes in adhesion are lesser in steam oxidised films as compared to hot water oxidised films.

It has been reported[99] that heat treatment at moderately low temperature can elliminate all trapped excess vacancies where by adhesion increases. This might be one of the reason of increase in adhesion of our Al_2O_3 thin films on heating.

4.6 DC RESISTANCE :

As seen from fig.3.5.1 the I-V characteristics of both types of Al_2O_3 films show a ohmic behaviour at low voltages (3 V) and an exponential trend at higher voltages (30V).

Fischer and Gilaever[100] have observed similar trend of ohmic behaviour at low voltages and exponential rise at higher voltages. They have used sandwich structure and have explained the effect due to the mechanism of tunneling. Though our films are planer, the mechanism of tunneling might be responsible for the films conducting properties.

At low applied biases if injected carrier density is lower than the thermally generated free carrier density, Ohms Law is obeyed. At higher fields, since the electron are transferred faster than they are thermally created, exponential effect results. Since the very process of Al_2O_3 formation involves water ambient, here is always a possibility of water present in the pores. The increased resistance (decreased current) of thinner films might be due to the reduced pore surface area available for the water adsorption during film formation.

Our refractive index studies show more porous structure for hot water oxidised films, which means more air gaps are present between the particle whereby current through the hot water oxidised films is lower than that for steam oxidised films. The conductivity of a porous film is determined by grain boundry scattering, diffuse scattering at grsin surfaces, and intergrannular tunneling. The intergrannular distance being lesser in steam oxidised films. The conduction might be more for these films, though very thin films (~ 700 A°) behave like hot water oxidised films. The electrical properties of the porous Al_2O_3 films also governed by surface conductivity. The various ambients acting as controllers of the surface conduction mechanism.

EFFECT OF HUMIDITY :

As already indicated, since both the steam oxidised and hot water oxidised Al_2O_3 films are highly porous, the electrical properties are expected to be humidity sensitive.

An increase in steady state current values i.e. decrease in resistance with increasing relative humidity (fig.3.5.2.2) can be explained by the increase in the steady state number of water molecules continously supplied to the film surface.

In the water vapour ambient the Al_2O_3 surface is hydroxylated[101,102]. The OH^- group are attracted to the cation Al^{+3} ion and H^+ ions are attracted to oxygen ions. The Al-OH groups or water molecules can dissociate to give proton which migrate across the surface[103]. The surface conductivity increases with the water content. Also at low relative humidity, water is first chemisorbed on the oxide surface and a proton hopping mechanism[51] between hydroxyl ions can explain conductivity while at high relative humidity the conduction is due to proton hopping between physisorbed water molecules. The activation energy required to dissociate water is lower than that needed to dissociate hydroxyl ions, resulting in higher conductivity at high relative humidity. As the relative humidity increases there is an increased thickness of the adsorbed water film. There is a vast difference in resistance between various thicknesses especially of steam oxidiesd films. The surface to volume ratio of films, might be different, though the porosity (graph 3.3.2 (b)) are almost same.

All the films reach a steady state value after about 8-10 minutes (fig.3.5.2.1). The almost steady state indicate the filling up of pores by water. It is felt that lower thickness (700 A°) steam oxidised films which behave like higher thickness hot water oxidised films; can be used for humidity sensor applications. On exposure to air after 180 minutes of humidity expcsure, the resistance increases and tries to reach the fresh film value. The steam oxidised films attains values near to fresh film values. The steam oxidised films attain steady state values within about 50 seconds where as the hot water oxidised films takes a longer tims. This reversibility seems to be a result of physical desorption.

Due to variation in the size and distribution of pores in the two types of films the resistance changes are different in magnitude though the basic character is same. On repeating moisture - air cycle a number of times (fig.3.5.2.4) equilibrium is attained faster.The repeated adsorption desorption of moisture from the pores, the desorption part not taking place completely. At around 100% relative humidity, the adsorbed water vapour in the pores is in a liquid like condition and forms a miniscus. The vapoue pressure over the miniscus is less than the saturated vapour pressure.Thus the water vapour does not evaporate during desorption until the external pressure is equal to the vapour pressure over the miniscus.

As already discussed the film material has OH radicals along the outer surface of its pore walls and hydrogen bond formation takes place due to moisture. During deposition this comparatively strong interaction between the adsorbate-adsorbent molecules, some of the strongly attached molecules would be unable to evaporate to as soon as water vapour pressure decreases. Peri and Hannan[93] have presented infra-red evidence for the occurance of undissociated water molecules at low temperatures and showed that during heat drying, water molecules which were not desorbed and removed from system reacts further to form surface hydroxyl group. This might be the reason, why on heating at 40°C after moisture-air exposure (fig.3.5.2.3) the resistivity increases further. As mentioned in chapter III art.3.5.2.3 the hot water oxidised films showed current readings out of range of the pico-ammeter used.

Though on heating to 40°C there is increase in resistance but on heating to 120°C there is decrease in resistance, the film attaining equilibrium after about 100 minites. Even the refractive index results (art.3.3.3.3) indicate different behaviour as compared to 40°C heating.

The infra-red data (fig.3.6.1) after moisture exposure confirm that steam oxidised films are more sensitive than hot water oxidised films.

From the above discussion of the various properties of steam oxidised and hot water oxidised Al_2O_3 films, one very important conclusion can be made that steam oxidised Al_2O_3 films with its high adhesion and almost same porosity as of hot water oxidised film can acts as a good humidity sensor.

4.7 CONCLUSION :

This work for the first time reports the properties of steam oxidised porous Al_2O_3 films with a view to study the feasibility of developing it as a thin film humidity sensor. The porous Al_2O_3 films obtained by hot water oxidation were also studied. The various properties studied are the Refractive Index, Adhesion, DC Resistance, IR + XRD studies. The hot water oxidised Al_2O_3 fillms though studied by few workers, the adhesion aspects has not been dealt by any of them.

Most of the reports on the properties (especially refractive index and electrical properties) of porous Al_2O_3 films are on films of thickness greater than 2000 A°. Our studies are all on films less than 2000 A°. We have found that, thinner films are quite useful for humidity sensing purpose. The refractive index and D.C. resistance of the resistor varies with humidity due to variation in amount of water vapour adsorbed. The adsorption isotherms of water vapour on $Al_2O_3 \cdot H_2O$ plays a important role in the performance of sensor. The porosity is attributed to the platelet like outword growth of the hydroxlated aluminium oxide film.The steam oxidised film undergoes a densification process and indicated by refractive index and packing density and adhesion data (Art. 3.3.1, 3.3.2, and 3.4.1).

This densification leads to the increased surface to volume ratio for the film. Hence it may absorbe more water. Due to this steam oxidised Al_2O_3 films of lower thickness can act as a good sensor comparable with Al_2O_3 films of thickness greater than 3000 A° obtained by other methods.

The XRD and IR spectra confirm the formation of Al_2O_3 film though XRD results show an ill defined crystal structure of the film indicating a porous structure. IR data shows absorption in 2500 cm^{-1} to 3660 cm^{-1} range as expected of hydroxylated Al_2O_3. Also steam oxidised film show large changes on exposure to moisture again confirm the utility of these films as moisture sensors.

The changes in response due to the thickness variation indicate the necessity of individual calibration of each and every sensor.

The high adhesion along with high sensitivity and low response time (refractive index and resistance) of the steam oxidised Al_2O_3 films indicate it has a good potential for development as a humidity sensor. The log scale variation of resistance with relative humidity could be used differential humidity control.

Work on the standardisation of deposition condition especially rate of steam passage, temperature of substrate etc. may improve the reproducibility of the sensor.

4.8 SCOPE FOR FURTHER WORK :

The effect of long term aging on the repeatability of various sensor properties has to be ascertained.

The hysteresis in refractive index and D.C. resistance due to increasing relative humidity and decreasing relative humidity cycle should be studied in detail.

A suitable electrode material for studying sandwiched capacitor structure of the steam oxidised Al_2O_3 sensor, should be attempted. If the lower electrode is Au, on oxidation in steam / hot water possibility of Au_2Al complex formation resisting further oxidation exists.

A substrate transmitting 1649 cm^{-1} should be tried out to find out the water absorption band and more systematic infrared experimentation at various relative humidity should be done.

More detailed interpretation on the high adhesion of steam oxidised films should be done by using non-destructive characterisation.