FABRICATION AND CHARACTERIZATION OF POROUS ALUMINA AND CADMIUM SULFIDE FOR OPTOELECTRONIC APPLICATIONS

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ABSTRACT OF THESIS

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In this research work, porous films on aluminum foil, with vertical through and through pores, were fabricated. The films were anodized at different applied voltages and the conditions were reported. In some cases, aluminum foil films were anodized under constant current conditions. Thicker aluminum films, referred to as aluminum tape in this thesis, were also anodized to get good porous films. While the porous alumina films using aluminum tape produced pores with good uniformity, the films did not produce through and through pores. Porous alumina films were also prepared on aluminum evaporated ITO substrate. The films on ITO substrate were different from the porous alumina films using aluminum foil/tape. In case of ITO substrate based films, an additional condition, temperature was also varied. The anodization process on ITO substrate based films was done at lower temperatures in order to reduce the effect of high currents on the process. The SEM images for different anodization conditions were compared and the porosity of films was calculated. CdS was electrodeposited inside porous alumina. D.C as well as a.c. voltages were applied and duration of the process was varied to study their effect on film morphology and the thickness of the deposited CdS. The current-voltage characteristics of the CdS-deposited alumina films were plotted and the phase of the electrodeposited CdS was found to be hexagonal using XRD.

KEYWORDS: Vertical through and through pores, porous alumina, anodization, aluminum evaporated ITO substrate, electrodeposited CdS.

Vivekanand Jayaraman
Date: 12/09/2004
FABRICATION AND CHARACTERIZATION OF POROUS ALUMINA AND CADMIUM SULFIDE FOR OPTOELECTRONIC APPLICATIONS

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12/09/2004
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FABRICATION AND CHARACTERIZATION OF POROUS ALUMINA AND CADMIUM SULFIDE FOR OPTOELECTRONIC APPLICATIONS

THESIS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the College of Engineering at the University of Kentucky

By

Vivekanand Jayaraman
Lexington, Kentucky
Director: Dr. Vijay P. Singh, Professor of Electrical Engineering
Lexington, Kentucky
2004
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Signed: Vivekanand Jayaraman
Date: 12/09/2004
For my parents and brother
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Chapter 1. Introduction

In recent years there has been substantial interest in the synthesis and characterization of nano-structured materials. Considerable change in the physical, chemical and optoelectronic properties exhibited by nanostructures is the reason for increased attention towards them. Crystals with dimensions in the nanometer regime show a band structure which is considerably different from their bulk counterparts. For example, nano crystals show an effective increase in band gap due to quantum confinement effects [1-3].

Thin-film anodized porous alumina templates have the potential for revolutionary impact in nano-structured solar cells and display devices. They can be used to create large, uniform, self-ordered nanoscale hetero-junctions. This system uses natural self-organization of the anodized porous alumina to create periodic arrays of nanoscale structures. When aluminum is anodized in a suitable acidic electrolyte under controlled conditions, it oxidizes to form a hydrated aluminum oxide containing a two-dimensional hexagonal array of cylindrical pores [4]. Electrodeposition of subsequent materials in the pores leads to the formation of individual devices, each isolated from the other by the insulating alumina matrix around it [5].

The advantages of this method are (1) Uniform pores with sub-micrometer to nanometer diameters (2) Arrangement of vertically directed pores with high aspect (depth/diameter) ratio at almost identical distance from each other (3) Ability to control diameter of pores by changing electrolyte composition and electrochemical processing regimes and (4) High reproducibility of the film structure for samples of large sizes. (5) Large scale fabrication of uniform nano-scale devices [6].

CdS is an n-type semiconductor and has wide applications in optoelectronic devices, especially as a window material in solar cells [7]. Recent studies in nanocrystalline CdS showed considerable improvements in band gap. It has been found that the band gap of CdS can be tuned in the range of 2.4 eV-4.0 eV by varying the size of CdS crystallites [8]. In a heterojunction solar cell, the window material should allow as much light as
possible onto the absorber layer. So, due to a higher band gap, nano CdS has the potential to be a better window material in solar cells. In this work CdS was electrodeposited in the alumina template. After the fabrication of films, the samples were characterized with SEM to know the morphology and particle size, XRD was performed on CdS electrodeposited in porous alumina to know the structure of the CdS, and I-V characterization of the films after deposition of the top and bottom electrodes.
Chapter 2. Theory

1. Theory of Pore Formation by Anodization

Nano-porous alumina films are being increasingly used as a template for fabricating nano-dots and nanowires. While widely invoked with many potential applications, this particular technique seems to be restricted to creating metal or semiconductor nano-dots within an insulating alumina matrix [9-10].

Anodization is a technique that can form large-area ordered arrays of nanoscale elements in which a metal (aluminum in this case) is submerged in an electrolyte and a current flowing through the electrolyte is passed from the anode (aluminum) to the cathode (platinum). This process causes aluminum (the anode of the circuit) to react with the ions in the electrolyte and be transformed into alumina (Al₂O₃). If a thin film of aluminum is anodized, the final product will be an alumina template with a self-ordered structure of hexagonal pores. The pores dimensions can be controlled by varying the anodizing voltage and electrolyte type and concentration [11]. The principal features of this technique are:

1) Uniform regular distribution of microscopic pores with sub-micrometer to nanometer diameter.
2) Arrangement of vertically directed pores with high aspect ratio (depth/diameter) at almost identical distance from each other.
3) Ability to control the diameter of cells and pores by changing electrolyte composition and electrochemical processing regimes.
4) High reproducibility of the film structure for large size samples.

2. Electric Current Through the Electrolytic Cell

The current flowing through a system during electrolysis involves (1) electronic conduction through the external connectors and the electrodes, (2) ionic conduction
across the solution between the electrodes, and (3) transfer of electrons across the electrode-electrolyte interface. A simplified picture of electronic conduction is the movement of electrons through a relatively rigid lattice of electrode ions and as such involves a little movement of matter. Dissolution of a solute in a solvent results in the dissociation of the salt into ions; electric conduction in the solution is the movement of these ions; the cations (positively charged) moving towards the cathode and anions (negatively charged) moving toward the anode. Ionic conduction, therefore involves a net transfer of matter. At the electrode-electrolyte interface there is a transfer of electrons (1) from the cathode to the electroactive species which is reduced and (2) to the anode from the electroactive species which is therefore oxidized [12-13].

3. Classification of Anodic Oxide Layers

Anodic oxide layers can be classified according to whether or not the electrolyte exerts appreciable solvent action on the material. When the material is dipped into an electrolyte which possesses little or no ability to dissolve the oxide, the anodic oxide coating is thin and nonporous; the oxide is formed rapidly and has a thickness proportional only to the applied voltage. A film of this type, for example when aluminum is dipped in boric acid or borate electrolyte, has unique electrical properties and has been extensively used in electrolytic capacitors and rectifiers [14]. The mechanism for oxide formation in this “barrier” or “blocking” type of oxide is relatively simple. Initially high current flows and the oxide is formed rapidly, but after a short duration the current flow decreases to a relatively steady state value and the coating is completely formed. Thickness is a function of applied voltage and can be increased only by increasing the applied voltage [15]. The low residual current represents, in part the “leakage” through constituent particles on which the oxide does not form, and as such varies with the material and the condition of the material under treatment.

When a material is dipped in an electrolyte that exerts appreciable solvent action on the oxide, a relatively high, steady current flow and continued oxide film growth is observed. The amount of oxide formed is generally a function of current, temperature and time,
although the final thickness of the oxide is also reduced by the solvent action of the electrolyte which is most pronounced at and near the outer surface of the oxide layer. A suitable example would be the use of sulfuric and chromic acids electrolytes in applications requiring resistance to wear and corrosion. The growth of the oxide layer in this case is more complex. A barrier layer of oxide starts to form like in the previous case but as soon as the oxide is formed, solvent action by the electrolyte also starts to reduce the thickness of the barrier [16].

Another case of anodization in electrolytes that attack oxide occurs in electro brightening treatments. The oxide dissolves about as fast as it forms with the result that at the end of the brightening treatment, only a very thin oxide layer remains. This simultaneous formation and rapid dissolution of oxide tends to smooth out the surface irregularities and thus produces a brightly highly reflective surface [14].

4. Formation of the Oxide Cell Structure

Considering the simultaneous dissolution and formation of oxide, it is possible to theoretically derive the basic structure of the porous type of an oxide. When the solvent action begins at a single point, the thickness of the oxide is reduced and the current flows to repair the damage to the oxide layer. This raises the electrolyte temperature at the point and more rapid solution of oxide occurs. This mechanism would perpetuate a pore once it is formed, although other factors may halt the formation of some pores and the start the formation of others [14, 17].

As current continues to flow through the single pore under consideration and the additional oxide forms, it becomes clear that an oxide cell will be created. As the voltage and current fields about a point tend to be spherical, the advancing front of the oxide cell would be spherical if the pore is a point source. Since the pore is of finite size however, the cell front will have the shape of a spherical section somewhat less that a hemisphere. The thickness of the oxide layer between the material and the pore base must be less than what would be observed is a less dissolving electrolyte because an appreciable current is
flowing. Also, the cell wall cannot be thicker because such thicknesses cannot form. Thus, as the oxide is formed, a cylindrical cell, having a roughly hemispherical end and a cylindrical pore will be formed [14].

In actual practice, a continuous compact oxide layer rather than isolated ideal cells is formed. Consequently, the changes in shape necessary to form a compact layer must be considered. At the start of the coating formation, the ideal cells probably do start to form, but if only the cylindrical cells were formed, intervening pillars of metal would remain. These pillars would still be in effective electrical circuit and, therefore, would be converted to oxide. Thus if we consider the oxide layer to be composed of close packed cylinders, that the final shape of the oxide can be realized.

In such a close-packed array of cylinders, each cylinder would have line contact with six surrounding cylinders, and between each group of three contacting cylinders there would be a triangular pillar of metal with concave surfaces. As these pillars are anodically converted into oxides, the metal would be consumed equally from each face under the influence of the current from the pores of the three surrounding cells. When all the metal pillars are consumed in this fashion the oxide layer will be continuous and the cells will have the form of hexagonal prisms rather than cylindrical prisms [14].

With the conversion of ideal cylindrical cell to the actual close-packed array of hexagonal cells, the shape of the pore would also change. As the array changes from cylindrical to hexagonal shapes and the intervening metal is consumed, appreciable current will flow and localized heating and relatively rapid solvent action will result. Inasmuch as the metal to be consumed between the cylindrical cells is not evenly distributed, current flow, heating and solvent action will be localized, and the pore will be enlarged in proportion to the amount of the metal consumed. Thus, the pore will no longer be cylindrical, but will have projections in all directions. The cross-section of this shape would be an elongated one, which would vary somewhat in shape depending on the size of the pore, and in certain cases could become star shaped. The relationship between the cylindrical structure and the hexagonal cell structure is shown in the figure 2.1.
Figure 2.1 Relation between ideal cylindrical oxide cells with cylindrical pores and close-packed hexagonal cells with elongated pores.

The change from isolated cylindrical cells to close-packed hexagonal cells also requires a change in the shape of the oxide cell where it contacts the metal. Metal toward the junction of three adjoining cells will be under the influence of current from the pores in these cells and would be converted to oxide more rapidly by virtue of the higher current density resulting from overlapping current fields. Consequently the front of a single cell in a close packed array will have a larger radius of curvature than that of a single isolated cell, and the cell front will have the shape of a spherical section somewhat less than a hemisphere [18].

Based on the above, it can be predicted that anodic oxide coating formed in an electrolyte that exhibits appreciable solvent action on the oxide is composed of close-packed cells of oxide, each of which has the shape of a hexagonal prism. Each prism has a spherical shaped end and contains a centrally located pore, elongated in cross-section. Through microscopic examination of different anodic oxides the above theoretical prediction has been observed.

5. Formation of Porous Alumina

Porous alumina films can be fabricated by the using metallic aluminum in an electrolytic process with aluminum as the anode in an electrolyte which partially dissolves it, for
example oxalic acid, phosphoric acid or sulfuric acid. When a potential is applied over a prolonged period of time, an ordered formation of porous alumina film is observed. In order to explain the self organization phenomena observed in porous alumina, the situation during steady state pore growth has to be considered. Pores grow perpendicular to the surface with equilibrium of field-enhanced oxide dissolution at the oxide/electrolyte interface and oxide growth at the metal/oxide interface [19]. While the latter is due to the migration of oxygen containing ions (O\(^{2-}\)/OH\(^-\)) from the electrolyte through the oxide layer at the pore bottom, Al\(^{3+}\) ions which simultaneously drift through the oxide layer are ejected into the solution at the oxide/electrolyte interface. The fact that Al\(^{3+}\) ions are lost to the electrolyte has been shown to be a prerequisite for porous oxide growth, whereas Al\(^{3+}\) ions which reach the oxide/electrolyte interface contribute to oxide formation in the case of barrier oxide growth [20]. The atomic density of aluminum in alumina is by a factor of two lower than in metallic aluminum. A possible origin of forces between neighboring pores is therefore the mechanical stress which is associated with the expansion during oxide formation at the metal/oxide interface [21]. Since the oxidation takes place at the entire pore bottom simultaneously, the material can only expand in the vertical direction, so that the existing pore walls are pushed upwards. Under usual experimental conditions the expansion of aluminum during oxidation leads to less than twice the original volume, since Al\(^{3+}\) ions are mobile in the oxide under the electric field, so partly the oxidized aluminum does not contribute to oxide formation.

While the pores nucleate at the surface at almost random positions, ordered pore domains of \(\mu\)m size were observed till the bottom of the layers [14]. The lattice constant within the ordered domains was approximately proportional to the voltage, in accordance with the literature, where proportionality of both pore and cell wall diameters to the voltage has been established. The quality of the ordering of this structure depends on the anodization voltage [22]. The best results were obtained for 40 V when oxalic acid was used as an electrolyte. This process of anodization of aluminum, leads to an ordered porous alumina array, with a barrier layer at the bottom. The barrier layer is defined as the nonporous layer found at the bottom of the pores. The barrier layer consists of a thin alumina layer on top of a comparatively thicker aluminum layer.
The anodization of alumina can be explained with the following equations:

\[ 2\text{Al} + (3\text{O}^\text{-})_{\text{ox}} = \text{Al}_2\text{O}_3 + 6\text{e}^- \]
\[ \text{H}_2\text{O} = 2\text{H}^+ + (\text{O}^\text{2-})_{\text{aq}} \]
\[ (\text{O}^\text{2-})_{\text{aq}} = (\text{O}^\text{2-})_{\text{ox}} \]
\[ \text{Al} = \text{Al}^{3+} + 3\text{e}^- \]

Figure 2.2 Schematic diagram of ordered porous alumina [23].

6. Factors Affecting Pore Formation

As the formation of the porous alumina membrane involves a balance between oxide formation and its dissolution, the formation of the oxide layer can only be as fast as the solution occurs at the bases of the pores [14]. In contrast to the formation of the alumina which is an electrochemical process, the dissolution of the top alumina layer is a chemical process. The balance between formation and dissolution of alumina is a rather complex process, because at least six major variables are involved: electrolyte type, electrolyte concentration, bath temperature, voltage, current density and time. Electrolyte type, concentration, and temperature, along with current density and voltage are interdependent, with the result that no variable can be changed without causing a change in at least one other variable [17]. Of the six major variables under discussion, time may
be eliminated by considering the rate of dissolution. Since the rate of dissolution of the alumina layer is a chemical process, current density does not have a direct effect on it, but will indirectly have an effect on the dissolution rate as it affects the temperature of the bath. Voltage will also not affect the rate of alumina dissolution directly, but will influence the rate of dissolution as it affects the current density and temperature. Thus, the dissolution rate of alumina layer is defined in terms of electrolyte type, electrolyte concentration, and the bath temperature, which are also the factors which affect the barrier layer thickness.

7. Factors Affecting the Barrier Layer Thickness

Considering the effect of the six major variables on the barrier layer thickness, time is not a factor because the barrier layer thickness remains constant with time, once the balance between the formation and the dissolution of the oxide has been established. With regard to the three variables, voltage, current density and the bath temperature, it has been found that they are interdependent, and that a change in one will be reflected in a change in one or both of them [17-18]. Hunter et al in their investigation found that the applied voltage had no effect on the unit barrier thickness. Unit barrier thickness refers to the barrier layer under a single pore. However the applied voltage does have bearing over the thickness of the barrier layer. Temperature has a much greater effect on unit barrier thickness, and decreasing temperature results in greater unit barrier layer thickness. This behavior would be expected as the solvent action of an electrolyte decreases with temperature.

The unit barrier thickness is not affected by current density either just like it is not affected by the applied voltage. Pronounced changes are seen in unit barrier thickness with variation in electrolyte concentration. At very low concentrations of the electrolyte the ability to dissolve the alumina layer and develop pores decreases to an exceptionally low level. At very high concentrations of the acid electrolyte, no alumina layer gets formed, because of high dissolution as well as insufficient amount of water present to ionize the electrolyte and form the oxide layer. As electrolyte concentration effects a change in bath temperature as well as sample thickness, the unit barrier thickness is also
affected by the temperature of the bath as well as the initial thickness of the aluminum film.

8. Porosity of the Anodized Film

An important factor in describing the structural features of the anodized alumina film is the porosity of the film, which is defined as the total volume of the pores divided by the total volume of the oxide. The porosity can also be expressed as the total area of pores per unit surface area of the anodized specimen, since the average pore radius, scarcely changes with the depth of the pores and the depth of the pores is nearly equal to the total film thickness [24-25].

It has been reported in some works that porous alumina membrane studies could also consider the thermal expansion of the membrane due to its formation as well as the chemical effect of anodization. The outer wall is anion-contaminated, whereas the inner layer consists of a dense pure alumina. In the case of a well defined self-ordered porous alumina, we observe always the same r/D, where r is the interpore distance and D is the pore diameter [26]. The porosity of a hexagonal structure is given by

\[ P = \frac{2\pi}{\sqrt{3}} \left( \frac{r}{D} \right)^2 \]

9. The Principles of Electrodeposition

Cadmium Sulfide was electrodeposited into the alumina pores through the process of electrodeposition. Electrodeposition involves the chemical phenomena associated with charge separation. This charge separation leads to charge transfer, which can occur homogenously in the solution, or heterogeneously in solution. In reality to assure electroneutrality, two or more charge transfer half-reactions take place in opposing directions. Except in the homogenous redox reactions, these are separated in space, usually occurring at different electrodes immersed in solution in a cell. These electrodes
are linked by conducting paths both in the solution and externally so that charge can be transported [13]. In the electrodeposition of CdS, the two electrode system was used. The two electrode system is similar to the anodization setup shown in figure 3.1. The two electrodes are called the working electrode and the counter electrode. Electrodeposition of the required material takes place on the working electrode. The potential is applied with respect to the counter electrode. The thickness of the deposited film is directly proportional to the applied potential as well as duration of electrodeposition. In case of d.c. electrodeposition the applied potential is the d.c. voltage applied across the counter electrode and the working electrode.

A step in applied potential or current represents an instantaneous alteration to the electrochemical system. Potential and current step give complementary information because, whereas in the first case the potential change causes a brief capacitive current peak, in the second case a part of the applied current, the value of which probably varies with time, is always used to charge the double layer as the potential changes. The study of the variation of the current response with time under potentiostatic control is called chromoamperometry. This potential step is the basis of pulse voltametry. Thus pulse voltametry is essentially repeated chromoamperometry [13]. In some cases, metal contacts were evaporated onto the electrodeposited CdS. In our device, ITO was used as the bottom contact whereas Au/Cu was used as top contact.

10. Metal-Semiconductor Interface

Knowledge of metal-semiconductor (MS) interface properties is important because the present day integrated circuits are connected to rest of the electrical circuit through these junctions. According to the Schottky theory the MS contact can be rectifying or ohmic depending on the type of semiconductor, work functions of metal and semiconductor. Some times the rectifying metal-semiconductor contacts are used in applications that require fast switching [27].
11. Schottky Barrier Diodes

The rectifying MS contacts are often known as Schottky diodes and the barrier formed between them as Schottky barrier. The Schottky barrier is known to appear at metal-semiconductor interface in the following two cases,

1. When $\phi_m > \phi_s$ and the semiconductor is n-type.
2. When $\phi_m < \phi_s$ and the semiconductor is p-type.

In this thesis document the discussion would be about the first case as the devices we would discuss are made with n-type semiconductor CdS and Au/Cu [28].

12. Energy Band Diagram of Metal and n-type Semiconductor

![Band diagram of metal and n-type semiconductor before contact.](image)

Figure 2.3 Band diagram of metal and n-type semiconductor before contact.

Figure 2.3 illustrates the energy levels of metal and semiconductor. The quantities $qX$, $E_0$, $E_f$, $E_{fm}$, $E_c$, and $E_v$ represent electron affinity of semiconductor, vacuum energy level, semiconductor Fermi energy level, metal Fermi energy level, conduction band and valence band respectively. When the metal and semiconductor are brought into an intimate contact, the electrons would diffuse from the semiconductor to the metal until the Fermi levels of both sides are aligned and the system reaches equilibrium. Now, as a result of this charge transfer, positive charge of width ($w$) is developed in the semiconductor and this charge is balanced by a sheet charge developed on the metal. This is similar to the depletion layer in the pn junctions. But in the case of Schottky
In Figure 2.4 a bend can be seen in the allowed energy levels of the semiconductor at the interface of metal and semiconductor. The charge exchange between semiconductor and metal will result in a field at the interface. The quantity $qV_{bi}$ in Figure 2.4 indicates the built-in potential and an electron can cross the barrier when it has a potential of $V_{bi}$. The term $q\phi_B$ represents the barrier height and is equal to $q(\phi_m - X)$ [29].

13. Depletion Region Approximation

The Depletion Region Approximation allows us to develop some useful relations by making some assumptions. Though these assumptions do not hold true for most real situations, they are fairly good approximations and will help us to have a better understanding of the devices.
These assumptions are,

1. The positive charge developed at the MS interface in the n-type semiconductor is only due to ionized donors. The concentration of free holes and electrons is considered to be zero for the region $0 < x < x_d$ (Figure 2.5).
2. For $x > x_d$, the donor density ($N_d$) is equal to free electron concentration ($n$) and the electric field ($E$) is zero [29].

### 14. Electrostatics of Schottky Diodes

In figures 2.5 and 2.7, the quantities $\rho$, $Q$ and $E(x)$ signify charge density, space charge and Electric Field [30].
Figure 2.7 Electric Field at MS Junction.

15. Electric Field $E(x)$

We know that

$$E(x) = -\frac{dV(x)}{dx}.$$  

Therefore

$$\frac{dE(x)}{dx} = -\frac{d^2V(x)}{dx^2}.$$  

But according to Poisson’s equation

$$\frac{d^2V(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon_s}.$$  

Thus we get

$$\frac{dE(x)}{dx} = \frac{\rho(x)}{\varepsilon_s} = \frac{qN_d}{\varepsilon_s}.$$  

Integrating the above equation we get

$$E(x) = \frac{qN_d (x - x_d)}{\varepsilon_s}.$$  

From figure 2.7 it is clear that $E_{\text{max}} = E(0)$.

So

$$E_{\text{max}} = E(0) = -\frac{qN_d x_d}{\varepsilon_s}.$$
16. Built in Potential \((V_{bi})\)

The built in potential can be calculated by integrating the electric field. So on integrating the electric field equation with limits 0 and \(x_d\) we get,

\[
V_{bi} = \frac{1}{2} \frac{qN_d x_d^2}{\varepsilon_s}
\]

If \(w\) is the depletion width then the above equation can be written as

\[
V_{bi} = \frac{1}{2} \frac{qN_d w^2}{\varepsilon_s}
\]

Hence we can write ‘w’ as,

\[
w = \sqrt{\frac{2V_{bi} \varepsilon_s}{qN_d}}
\]

17. Space Charge \((Q_s)\)

From figure 2.6 we can write the space charge per unit area in semiconductor as

\[
Q_s = qN_d x_d = qN_d w
\]

Thus we get,

\[
Q_s = \sqrt{2q \varepsilon_s N_d V_{bi}}
\]

18. Schottky Diodes Under Bias

On applying bias to a Schottky diode the device would be in non equilibrium and the band diagrams would be different from that of equilibrium conditions. When the metal is biased positive with respect to semiconductor; then there would be a potential drop across the barrier and the diffusion current increases exponentially with bias. For this reason the built in potential gets modified as \(q(V_{bi}-V_a)\); where \(V_a\) is the applied voltage. This case is termed as forward bias and figure 2.8 shows the corresponding band diagram.
In the case of reverse bias (metal biased negative with respect to semiconductor) the built in potential however increases by $qV_a$. Figure 2.9 illustrates the band diagram for reverse biased conditions where the built in potential is $q(V_{bi}+V_a)$ [30].

**Figure 2.8** Band Diagram of Schottky diode for forward bias conditions.

**Figure 2.9** Band Diagram of Schottky diode for Reverse bias conditions [31].
Chapter 3. Experimental Procedure

1. Fabrication of Porous Alumina

In recent years, there has been increasing interest in the fabrication of nanometer-sized fine structures based on their potential applications in electronic, optical and micromechanical devices. One approach to the fabrication of nanometer-sized structures is to use a naturally occurring structure as a host for fabrication. This approach is promising, especially for the preparation of large-area, nanometer-sized structures with high aspect ratios, which are difficult to form by a conventional lithographic process [32]. Anodic porous alumina, prepared by the anodic oxidation of aluminum in an acid electrolyte is one such self-organized structure with nanohole arrays.

Anodic aluminum oxide (AAO) films grown in strong acid electrolytes possess very regular and highly anisotropic porous structures with pore diameters, ranging from below 10 to 200nm, pore lengths, from 1 to 50µm, and pore densities in the range $10^9$-$10^{11}$cm$^{-2}$. The pores have been found to be uniform and nearly parallel, making AAO films ideal templates for the electrochemical deposition of fairly monodispersed nanometer-scale particles. In using templates to produce nanostructures, one must take into account the template’s chemical stability, its insulating properties, the minimal diameter and uniformity of the pores, and the pore density. Pore sizes small enough to ensure the observation of quantum size effects in the deposited structures are not readily available with commercial anodic aluminum oxide membrane.

High purity aluminum sheets were cut into 1 ” x ½ ” and degreased by dipping in acetone solution followed by rinsing in de-ionized water for several seconds. Anodizing was performed at constant voltages as well as constant currents on different substrates for a sufficient time to develop steady-state morphology in different concentrations of sulfuric acid as well as oxalic acid solutions. Pore opening was done after anodization to increase the pore size as well as the barrier layer. The process of pore opening involves dipping the foil in a solution with less oxide dissolving ability than the anodizing electrolyte. A
mid solution of phosphoric acid or chromic acid depending on the substrate was used for pore widening. Reanodization was conducted in order to improve the regularity of the pores [33]. Reanodization was done with the same condition as the initial anodization. Reanodized films have been reported to have better controlled pore sizes with less variation in mean diameter. The temperature and concentration of anodizing electrolytes used in the present work are based on conventional conditions.

2. Setup for Anodization

Anodization of aluminum involves a simple setup of 2 electrodes in the electrolyte of suitable concentration. The designed setup in our laboratory can be cooled as well as heated depending on the requirements. In case of anodization of aluminum evaporated onto the ITO/Glass substrate, the electrolyte was cooled to as low as 2°C, while the pore opening solution was heated to as high as 60°C when chromic acid was used. Thus the setup for anodization was designed to be simple, so that it could easily cooled or heated depending on our requirements.

![Diagram of setup for anodizing alumina.](image)

Figure 3.1 Diagram of setup for anodizing alumina.

3. Porous Alumina from Aluminum Tape

A thick high purity Aluminum tape was commercially purchased. The thickness of this tape was estimated to be 25µm. Prior to the fabrication of the porous alumina, the aluminum tape which was glued on one side was cleaned thoroughly. Cleaning is an
essential step for obtaining smooth and contaminant-free films. Initially the substrates were placed in a beaker of acetone and sonicated for 10 minutes. Later the substrates were rinsed in de-ionized water. Finally the samples were dried with flowing nitrogen. This process, while removing most of the grease from the aluminum surface, is likely to leave traces of glue behind. It is assumed and seen from SEM images that pore formation takes place from the non-greasy side.

After degreasing, the aluminum tape was used as the anode in the setup in figure 3.1. A platinum sheet, 25mm x 25mm x 0.5mm thick, was used as the cathode. The anodization was done at room temperature in a solution of 0.3M oxalic acid. The anodization was done for durations of 40 and 50 minutes on different substrates. The current density after the initial transients remains stable throughout the process. This leads to smoother formation of pores, as it can be assumed that the electric field intensity remains constant almost throughout the process, because it has been shown previously that the electric field intensity is proportional to the log of observed current.

Pore opening was done for duration of 2 minutes in a solution of 7.5% (volume) phosphoric acid at 45°C. Pore opening reduces the barrier layer as well as increases the size of the pores. Pore opening is preferred in phosphoric acid medium as it is a milder dissolving solution of aluminum, compared to oxalic acid. At the end of the pore opening stage we can clearly see the formation of white spots appear on top of the tape to indicate the formation of porous alumina. In case of aluminum tape samples which were anodized for duration of 50 minutes, broken pieces were observed on the surface indicating over-etched porous alumina.

4. Porous Alumina from Aluminum Foil

Aluminum foils of lower thicknesses than the aluminum tape were commercially purchased. Aluminum foils of thicknesses 4µm, 2µm and 1.5µm were used. These foils did not have glue on either side. However cleaning of the foil was essential to remove the impurities on the foil. Initially the substrates were placed in a beaker of acetone for
duration of 30 minutes. Later the substrates were rinsed in de-ionized water. Finally the samples are dried with flowing nitrogen. It was observed the samples split to smaller pieces when sonicated. Hence the samples were degreased in acetone but were not sonicated during the process.

After degreasing, the aluminum foil was anodized by using it as the anode in the setup in figure 3.1. A platinum sheet was used as the cathode. The anodization was done at room temperature in a solution of 0.3M oxalic acid. The anodizations were done for varying durations of time. The applied voltages were varied to observe the effect of applied voltage on the final pore size of the porous alumina film. The current density after the initial transients remains fairly stable; however there is a slight variation of current throughout the process. This leads to the formation of ordered pores, however the film morphology would be considerably better if the currents were as stable as those observed in the case of anodization of aluminum tape.

Pore opening was done for duration of 3 minutes in 7.5% phosphoric acid at 45°C. Pore opening was also done for duration of 2 minutes in the same electrolyte in one particular case. It was observed that while pore opening plays a major role in the removal of the barrier layer, a small variation in etch time does not lead to a significant change in the morphology of the film. It is presumed that a change in pore opening temperature would lead to a considerable change in the film morphology, as the electrolyte dissolvability as well as ion mobility in the electrolyte increases with increase in temperature.

A 2-step anodization process is often preferred over 1-step anodization, as it produces more ordered pore growth [4, 34]. In case of 2-step anodization, the substrate is re-anodized in the same solution as it was originally anodized. In the case of aluminum foil, it was re-anodized in 0.3M oxalic acid for varying durations of time on different samples. It was observed that the best samples were obtained when the sample was reanodized for 5 minutes. The change in porosity as well film morphology is clearly observed for different re-anodization times.
Constant current anodization was also used on some samples. In this case the current through the anodizing circuit was kept a constant throughout the process. The corresponding voltages across the electrodes were noted at different times. Constant current anodization processes used the 2-step anodization method. The film morphology of the constant current anodized films was found to be different from constant voltage anodized films. However the curvature of the voltage-time curves observed in case of the constant current anodized films was similar to the curvature of the current density-time curve observed in constant voltage anodized films.

5. Porous Alumina from Aluminum on ITO/Glass Substrate

The ITO/Glass substrate was commercially purchased from Delta Technologies. The substrate was initially placed in a beaker with acetone and sonicated for a duration of 10 minutes. Later the substrates were rinsed in de-ionized water and transferred to a beaker of methanol, in which they were sonicated for 10 minutes, and this process was repeated with de-ionized water. Finally the samples were dried with flowing nitrogen. In some cases the ITO/Glass substrate was plasma etched in a PE-CVD chamber in the presence of oxygen gas. The samples were plasma etched in order to improve grain boundaries of ITO, so that the subsequently deposited aluminum would be much more uniform. However the etching for 30 minutes did not significantly improve the anodized alumina morphology.

Aluminum was deposited on the ITO/Glass substrate by thermal evaporation of aluminum coils. Thermal evaporation is one of the physical vapor deposition techniques and essentially involves passing current through the source material in a vacuum chamber. The source material is either placed on a filament or in a boat made with a material possessing higher melting point than the material to be deposited. A tungsten filament was used and the pressure in the chamber was maintained close to $2 \times 10^{-6}$ Torr. Current of order of 2A was passed through the filament or boat. The target substrates were placed on a disc above the source material. When the high current is passed through the boat, the source material vaporizes and deposits on the substrates above. The current
is increased in steps to prevent breakage of the filament or boat. For every step of the current increase, the pressure in the chamber may raise due to the vapors developed. Each step of the current increase is done only after the pressure in the chamber stabilizes. Higher vacuum in the chamber is required for a uniform film deposition. In the absence of vacuum the vapors may get deflected and the deposited film would not be uniform. Further, vacuum avoids the oxidation of the source material. Aluminum of thicknesses 800nm, 1µm and 2µm was deposited on the different substrates. Aluminum can also be deposited on ITO/Glass by e-beam evaporation as well as by sputtering. Aluminum deposited by the different techniques would be slightly different in particle sizes as well as adhesion on the substrate.

After the evaporation of aluminum onto the ITO/Glass substrate, the sample was annealed. Annealing basically involves heating of the film in a furnace. This process improves the film adhesion and grain size. Aluminum films deposited thermally on ITO/Glass substrate were annealed in a quartz furnace tube under a nitrogen flow. Annealing was done for 1 hour at a temperature of 400°C. Nitrogen flow is essential to prevent the oxidation of aluminum at high temperatures.

After the evaporation of aluminum onto the ITO/Glass substrate, the sample was annealed. The annealed aluminum would have better adhesion to the ITO/Glass substrate than the unannealed films, and would be able to withstand the anodization process much better. After annealing the samples were then cleaned to remove all impurities by being placed in a beaker of acetone for duration of 30 minutes. Later the samples were rinsed in de-ionized water. Finally the samples were dried with flowing nitrogen. The samples were degreased in acetone but were not sonicated as sonication seemed to cause cracks on the aluminum surface.
Figure 3.2 Diagram of setup for anodizing aluminum evaporated on ITO glass.

After degreasing, the aluminum evaporated on ITO/Glass substrate was used as the anode in the setup in figure 3.2. A platinum sheet was used as the cathode. The anodization was done at different temperature in different solutions of varying molarities. Sulfuric acid and oxalic acid were used as electrolytes. As the dissolubility of aluminum in sulfuric acid is higher than its dissolubility in oxalic acid, the samples were anodized at lower voltages in sulfuric acid than in oxalic acid. Since the conductivity of ITO/Glass substrate is higher than the normal aluminum tape or foil, the observed currents would be considerably higher for similar conditions as the anodized samples of aluminum foil. Hence, the process of anodization of aluminum deposited on ITO/Glass substrate was done at lower temperatures. The temperature of the electrolyte was lowered by keeping it in a ice and salt solution. The anodizations were done for varying durations. The current density shows variations throughout the process, except in the case of sample anodized in 3% wt oxalic acid at 2°C. This causes the formation of pores in some cases, with cracks as well as voids in some cases and non formation of pores in some cases.

Pore opening was done for different duration times in a solution of chromic acid at 60°C. Pore opening reduces the barrier layer as well as increases the size of the pores. Chromic acid solution was prepared with 5% H₃PO₄ and 2% CrO₃ [35]. Chromic acid was chosen for pore opening process instead of phosphoric acid, as it etches the alumina at a slower rate than phosphoric acid and thus causes less damage to the surface morphology of the films. At the end of the pore opening stage we did not see the formation of clear white spots as observed in the case of aluminum tape and foil. This indicates that the formation of pores is not complete in the case of aluminum on ITO/Glass substrate. In order to observe the spots, pore opening for varying durations was tried, but they could not be
observed. Another approach could be to increase the temperature at which pore opening was done.

Both 2-step anodization as well as 1-step anodization was used for anodization of alumina from aluminum on ITO/Glass substrate. The initial anodization times as well as the re-anodization times were varied to get porous alumina film. The aluminum on ITO/Glass substrate was re-anodized in electrolyte acid solution for varying durations of time on different samples. However a significant change in film morphology was not observed when the 2-step anodization was used instead of single anodization procedure. But in case of 2-step anodization in 3% wt oxalic acid solution at 2°C at 40V, the observed currents were stable after the initial transients. The anodization was for a duration of 2 minutes followed by pore opening for 3 and ½ minutes followed by reanodization for 24 ½ minutes.

6. Sample Preparation for Electrodeposition of CdS in Porous Alumina

![Figure 3.3 Setup for CdS electrodeposition on Al foil.](image)

Porous alumina prepared from 4µm thick aluminum foil was used for electrodeposition of CdS. The samples for electrodeposition were prepared by anodizing for 25 minutes followed by pore opening for 3 minutes and re-anodized for 5 minutes. The prepared sample along with ITO/Glass was used as the working electrode in the setup shown in figure 3.3. Platinum was used as the counter electrode in the process. Different methods were tried to improve the ITO/Glass and alumina foil contact. In the first few
experiments ITO/Glass and alumina foil were held together with a single clip. Silver paste was applied between ITO/Glass and alumina foil in the next case. In later case epoxy was used between ITO/Glass and alumina foil. In case of silver paste applied working electrode, the silver paste could not hold the foil and ITO/Glass together at high temperature, and with metal epoxy the CdS deposition was only along the walls. Recently, this setup was modified by sputtering ITO on one side of the anodized porous alumina foil, and thermal joint compound was applied on the sputtered ITO side.

7. Electrodeposition of CdS in Porous Alumina

Cadmium Sulfide is a II-VI semiconductor with many optoelectronic applications. CdS has been extensively used in solar cells along with CdTe and CIS. The electrodeposition of CdS in the porous alumina for future optoelectronic applications was considered as the logical extension for this project. The electrodeposition of CdS was followed by deposition of suitable contacts for current-voltage measurements on some samples.

CdS nanocrystals were prepared by electrochemical deposition in dimethyl sulfoxide (DMSO) solution composed of 0.055 M CdCl$_2$ and 0.19 M elemental sulfur [36]. The temperature was maintained at 120°C with a hot plate. A 10 V dc voltage was applied between the alumina and ITO/Glass working electrode and platinum counter electrode from 5 to 30 min. This dc electrodeposition method was used because of its simplicity as well as the uniform deposition on flatter substrates. This method was initially used for electrodeposition of CdS. When electrodeposition was done at 10V for a duration of 8 minutes, CdS deposited into some of the pores. However as the SEM image of this condition in figure 4.26a clearly shows under-deposition of CdS in the pores. When the duration of CdS deposition was increased to duration of 30 minutes considerable over-deposition was observed as seen from the SEM image in figure 4.27a. When the contacts were changed from simply the top clip to silver paste between the ITO/Glass and alumina foil or the application of metal epoxy did not result in significant improvement in deposition of CdS in porous alumina foil. In the case of silver paste, because of high
temperature of the electrolyte solution the silver paste could not hold the ITO/Glass and alumina foil together but instead dissolved in the electrolyte solution.

In the case of porous foil, it has been reported that electrodeposition by dc is very unstable and uniform filling cannot be achieved due to a cathodic side reaction which leads to the local deposition in single pores. Hence pulsed electrodeposition was tried as an alternate method for CdS deposition in porous alumina. Pulsed electrodeposition is reliable for deposition into high aspect materials and compensates for slow diffusion driven transport into the pores. For pulsed deposition, the porous alumina foil was sputtered with 90nm of ITO on one side. Thermal joint compound was applied on the sputtered side of the alumina foil. The alumina foil was used as the working electrode, and platinum was used as the counter and reference electrode. The electrodeposition was carried out with a pulse of high of -2V and a low of -2.5V. The electrodeposition was done for 15 cycles; each cycle had 20 seconds of high pulse time and 20 seconds of low pulse time with 20 seconds of quiet time. From the SEM image in figure 4.30a, it can be concluded that CdS uniformly deposited into the pores of the alumina foil. However it also deposited slightly more than the pore height. Thus it can be deduced that with lower deposition time, or with smaller applied pulse voltage under-deposition of CdS into the pores could be achieved. It has also been reported that pulsed deposition current pulses if applied, would allow better control over the deposition parameters, such as deposition rate and ion concentration at the deposition interface.

8. **Field Emission Scanning Electron Microscope (FE-SEM) Imaging**

FE-SEM uses a beam of electrons generated by a field emission source to scan the surface of the sample. These electrons are generated in an electron gun and are accelerated in a column with a high electrical field gradient. The electron gun is usually housed on top of the column and the column is maintained in vacuum to prevent any deflection of electrons. When the electrons bombard the sample, a variety of signals are generated. These include secondary electrons, back scattered electrons, light, heat and transmitted electrons. Secondary electrons are the electrons from the sample while
backscattered electrons are the one that bounce off the nuclei of atoms in the sample. There would be a detector for secondary electrons which catches them and produces an electronic signal. Surface structure of the sample can be understood from the angle and velocity of the secondary electrons. Further, the signal is processed with amplifiers and is finally seen as a image on a monitor [37].

**Sample Preparation**

The test sample needs to be mounted on a copper stub available specifically for SEM imaging. Prior to sample preparation, the copper stubs were thoroughly cleaned with acetone and DI water. Sometimes the stubs might be scrubbed with Kimwipes if sonication does not clean them completely. Later they are dried in flowing air or nitrogen. Then a conducting graphite tape of the dimensions 2 mm x 6 mm is cut and stuck on the copper stub. It is important to make sure that the tape sticks smoothly without any undulations. The test sample is cut into dimensions smaller than 2 mm x 6 mm using a diamond scribe and is placed on the graphite tape. Also, the sample is pressed with a tweezer to make sure it sticks firmly to the tape. Now a thin paint brush is used to coat the edges of the sample with conducting colloidal graphite. Further, the samples are coated with gold/palladium to increase conductivity before placing them in the SEM chamber.

**Specimen Exchange**

During this process the specimen exchange chamber is isolated from main chamber so that air does not enter the main chamber. The specimen holder is removed from the specimen exchange chamber according to the standard procedures. The specimen holder has a set of grooves to hold the stub. The required groove is chosen depending on the substrate thickness and imaging requirements. Once the stub is placed in the proper groove, it is moved with a pair of tweezers to confirm that it is not held loosely. Now the specimen holder is replaced into the specimen exchange chamber by following the standard procedures.
SEM Imaging Procedures

The sample is initially brought into standard position. The sample is focused with low magnification and then in high magnification. At low magnification a small object is focused. Then the object is moved to center of the screen and the magnification is increased. Next, the aperture align switch is turned on. If there is any horizontal or vertical swing, the aperture alignment is corrected with the screws provided on the aperture holder until the swing disappears. Now the image can be sharpened by using the X and Y stigmator controls. The focus and stigmator controls are switched until the sharpest image is obtained. Now the image is ready to be captured and could be saved in a computer file.

The above mentioned SEM image was used to image each procedure. The captured image was used to estimate the formation of films. The porosity of the anodized alumina was also estimated from the SEM images. The SEM images help us in comparing the morphology of the films with changes in applied voltage/current.

9. X-Ray Diffraction (XRD)

The interaction of X-rays with a crystalline material results in a diffraction pattern which is usually known as XRD. This pattern is unique to each material and when a mixture of materials is exposed to the X-rays then each produces a pattern of its kind. XRD therefore provides valuable information about the phase, the structure and the composition of the sample under test [38].

Usually in a crystal the X-rays are diffracted by a series of parallel planes. Orientation of these planes is defined with Miller indices h, k and l which are integers. If a, b and c are considered to be axes of the unit cell then h, k and l would cut the axes a, b and c into h, k and l sections respectively. If d is the spacing between the parallel planes then the
constructive interference would occur at an angle of incidence $\theta$ which satisfies Bragg’s law (equation 3.1).

$$2d \sin \theta = n\lambda \quad (3.1)$$

Where $n=$ integer and $\lambda=$ wavelength of the x-rays.

The XRD pattern obtained for a sample shows the peak intensities at $2\theta$ positions corresponding to the d-spacing among the planes in the crystal. This would let us know the indices of the planes and the phase of the material could be estimated by comparing with previously calculated reference. The diffraction patterns of most of the available materials is recorded and standardized. When a material is characterized with XRD, the results are compared with a standard set of data and the material can be identified.

XRD pattern was used to determine the orientation of porous alumina and electrodeposited CdS. The peak intensity at $2\theta$ position for porous alumina was observed at $45.4^\circ$ and electrodeposited CdS had peak intensities at positions of $25.16^\circ$, $26.8^\circ$, $28.44^\circ$ and $37.12^\circ$ corresponding to the planes (100), (002), (101) and (102) respectively. Thus, the XRD pattern indicates an hexagonal phase for CdS according to the 10-0454 JCPDS.

10. Electrical Characterization of Electrodeposited CdS

The samples which were initially electrodeposited at an applied voltage of 10V d.c. where ITO coated glass and alumina foil were held only by a single clip, were used for current-voltage characterization. In these cases, ITO was sputtered on one side, and on the other side gold or copper was deposited as contact. This method is similar to the aluminum deposition except for a tungsten boat being used instead of a tungsten filament. Also in case of copper deposition, copper powder was used in the boat and gold pellets were used for gold deposition. The pressure in the chamber was $2 \times 10^6$ Torr and the current passed was of order 2 A and 6A in case of copper and gold deposition respectively. The gold/copper contacts made were circular in shape and have a diameter of 2 mm. This is done by using a mask made with Al foil.
11. I-V Measurement Setup

I-V measurements on the devices were performed using two Keithley Digital Multi Meters and a DC power supply. The circuit diagram is depicted in figure 3.4. These instruments were interfaced to a computer and measurements were recorded by a program written in the Lab View software. I-V sweep and delay time were also controlled with the software. Measurements were made within a voltage range of -1V to +2.5V with a delay time of 1 second.

![Circuit Diagram for the I-V measurements.](image)

The observed I-V characteristic was found to be different in case of gold contacts than in the case of copper contacts. While a linear behavior was observed in the case of gold contacts, a high series resistance diode behavior was observed in case of films with copper contacts.
Chapter 4. RESULTS

1. Porous Alumina from Aluminum Tape

Pores as seen from the SEM images in figures 4.1a and 4.2a extend throughout the film from the barrier layer to the outer surface, pore cessation, division or merging being relatively rare under steady state conditions. In a plane view of the outer film surface, the pore diameters for the experimental condition were found to be 75nm and were approximately circular. No variation in texture of the inter-pore oxide was detectable for the relatively mild anodizing condition in the electron micrographs. While the film shown in figure 4.1a (device # 081003_1) has uniform pores, the film in figure 4.2a (device # 080403_2), is observed to have ruptured pore walls due to over-etching of the film.

For each SEM figure the corresponding figure on the right shows a typical current density – time characteristic for constant voltage anodization in oxalic acid. For constant voltage anodization, the current across the anode and cathode is inversely proportional to the device resistance. Thus, as observed from figures 4.1b and 4.2b, the current decreases during the first few seconds when the high resistance barrier layer is formed. Next as the pores start to develop, the current remains constant and the pores propagate. After anodization, a pore widening step was performed on all films of anodized alumina for 2 minutes. The purpose of pore widening is to remove impurity ions left over after the anodization process. The pore widening step removes a thin layer of the alumina, thus widening the pores to some degree. In figure 4.1, the sample (device # 081003_1) was more uniform than the sample shown in figure 4.2a (device # 080403_2) due to over anodization of the latter.
Figure 4.1 Aluminum tape (~25µm thick) was anodized in 0.3M oxalic acid at 40V for duration of 40 minutes followed by pore opening for 2 minutes at room temperature. The film shows 75 nm pore openings; it is very uniform due to the relatively long period of anodization as well as the use of 2 step anodization processes.

Figure 4.2 Aluminum tape (~25µm thick) was anodized in 0.3M oxalic acid at 40V for duration of 50 minutes followed by pore opening for 2 minutes at room temperature, also shows 75 nm pore openings. However the pore walls have ruptured at some places due to over-etching.
2. Formation of Alumina Template from Aluminum Foil

The homogeneity of cell size could be attained and domains of self-ordered cell arrays in the same direction appeared when anodizing voltage was 40 V, but just under the critical voltage of extremely high current. The sample shown in figure 4.3a (device # 080604_1) is observed to have less uniform pores, because the applied voltage is 20V which is less than the critical voltage for oxalic acid as electrolyte. The corresponding figure in 4.3b shows current density vs. time transients during constant-voltage anodization in oxalic acid solution. In case of samples anodized at 40V the relatively stable J-t curve seen is typical of curves obtained during steady porous film growth. With increasing anodization voltage, current density is increased. When the anodization voltage exceeded the value of critical voltage for self-ordered pore formation, i.e., at 40 V for oxalic acid, a high current accompanying intense gas evolution at the entire surface was observed. In these cases, film growth is not uniform over the entire specimen surface. When anodized at voltages less than the critical voltage, irregular film growth is observed due to low current density. As can be seen from the SEM images in figures 4.3 (device # 080604_1), 4.4 (device # 080202_2), 4.5 (device # 090203_2) and 4.6(device # 080604_2), the most homogenous films are observed when the applied voltage is close to the critical voltage, which is 40V in case of oxalic acid as shown in figure 4.5.

![Current density vs time plot](image)

**Figure 4.3** Aluminum foil (~4µm thick) was anodized in 0.3M oxalic acid at 20V for duration of 25 minutes followed by pore opening for 3 minutes, and reanodization for 5
minutes at room temperature. Pores of diameter 25nm approximately can be seen from the SEM image. The film is not very uniform because the applied voltage is much less than the critical voltage for anodization.

**Figure 4.4** 4µm thick aluminum foil was anodized in 0.3M oxalic acid at 30V for duration of 25 minutes and pore opening for 3 minutes, followed by reanodization for 5 minutes. Although the median pore size in figure 4.4 is approximately 25nm, many pore walls have collapsed, giving the appearance of larger pores.

**Figure 4.5** 4µm thick aluminum foil was anodized in 0.3M oxalic acid at 40V for duration of 25 minutes and pore opening for 3 minutes, followed by reanodization for 5 minutes. The SEM image shows the formation of pores of 45nm diameter approximately.
Figure 4.6 Aluminum foil (~4µm thick) was anodized in 0.3M oxalic acid at 50V for duration of 25 minutes followed by pore opening for 3 minutes, and reanodization for 5 minutes at room temperature. Pores of diameter 45nm approximately can be seen from the SEM image, but the structure is not well-ordered due to too high an etch rate.

Decreasing current at the end of step 2 shows anodization going towards completion. Reanodization for 5 minutes shows pores which are more ordered than in the 2.5 minute case. The pores of the 5 minute case are not as closely spaced as in 7.5 and 10 minute cases, but without erosion between pores. Thus while long duration of anodization is beneficial for pore formation, the time of anodization is dependent on the thickness of the foil. Thus comparing the SEM images of figures 4.5(device # 090203_2), 4.7(device # 083003_3), 4.8(device # 090203_3)and 4.9(device # 090303_1) we can conclude that for 4µm thick foil samples the best results are obtained when reanodized for 5 minutes as in figure 4.5. In figure 4.10(device # 090403_2) the sample was anodized for 25 minutes followed by pore opening of 2 minutes and reanodization of 4 minutes. The film shows very similar characteristics to the sample in figure 4.5(device # 090203_2), thus we can conclude that pore opening in phosphoric acid reduces the barrier width but a small change in pore opening does not significantly affect the pore dimensions. In figures 4.11(device # 020804_3) and 4.12(device # 021604_1) aluminum foil of thickness 1.5µm approximately was used for anodization in 0.3M oxalic acid at room temperature. The
sample shown in figure 4.11(device # 020804_3), was anodized at a constant voltage of 40V, while the sample shown in figure 4.12(device # 021604_1) was anodized by keeping the current through the film a constant of 12.4002 mA/cm$^2$. Thus while constant voltage anodization produced through and through pores, it would require longer reanodization time to get through and through pores in anodization with current through the film as constant. However, the pore walls are thinner in the case of sample in figure 4.12(device # 021604_1) than the sample in figure 4.11(device # 020804_3). Similar processes were tried on samples in figures 4.13(device # 012804_1) and 4.14(device # 013004_1) where the thickness of films were 2µm approximately. The sample in figure 4.13(device # 012804_1) was anodized at a constant voltage of 40V, the anodized film had similar morphology as the sample in figure 4.11 with a little less variation in pore dimensions. The sample in figure 4.14(device # 013004_1) was anodized by keeping the current through the film a constant of 12.40 mA/cm$^2$. However the film deteriorated to form large cracks.

Figure 4.7 Aluminum foil (~4µm thick) was anodized in 0.3M oxalic acid at 40V for duration of 25 minutes followed by pore opening for 3 minutes, and reanodization for 2.5 minutes at room temperature. Pores of diameter 45nm approximately can be seen from the SEM image. The pores while being throughout the film are not ordered and the pore walls are slightly thicker than the anodized film in figure 4.5.
Figure 4.8 4µm thick Aluminum foil was anodized in 0.3M oxalic acid at 40V for duration of 25 minutes followed by pore opening for 3 minutes, and reanodization for 7.5 minutes at room temperature. Pores of diameter 45nm approximately can be seen from the SEM image. While the pore density is higher than in figure 4.5 (5 minute reanodization), the pore walls became thinner and several of them have broken.

Figure 4.9 4µm thick Aluminum foil was anodized in 0.3M oxalic acid at 40V for duration of 25 minutes followed by pore opening for 3 minutes, and reanodization for 10 minutes at room temperature. Pores of diameter 45nm approximately can be seen from the SEM image. While the pore density is higher than the films in figure 4.5, 4.7 and 4.8,
many more pore walls are broken. Thus it can be concluded the film was over etched when reanodized for 10 minutes at 40V.

Figure 4.10 4µm thick Aluminum foil was anodized in 0.3M oxalic acid at 40V for duration of 25 minutes followed by pore opening for 2 minutes, and reanodization for 4 minutes at room temperature. Pores of diameter 45nm approximately can be seen from the SEM image. The results of this trial are very similar to the 5 minute reanodization, 3 minute pore opening case in figure 4.5. Thus we can conclude that while pore opening time is important for varying pore size, it requires a big variation in etch time to see a major change in pore size. Also a small change in pore opening time does not lead to any major change in film morphology.

Figure 4.11 Aluminum foil of thickness 1.5µm was anodized in 0.3M oxalic acid for duration of 25 minutes followed by pore opening for 3 minutes followed by reanodization
for 5 minutes at 22°C. This potentiostatic anodization at constant voltage of 40V produced through and through pores. However because of low thickness the pore size variation is greater than the film in figure 4.5. The median pore size was approximately 45nm.

Figure 4.12 Aluminum foil (~1.5µm thick) was anodized in 0.3M oxalic acid for 25 minutes with pore opening for 3 minutes followed by reanodization for 10 minutes. This galvanostatic anodization with a constant current of 40mA shows an incompletely etched barrier layer. Thus while potentiostatic anodization produced through and through pores, it would require longer reanodization time to get through and through pores in galvanostatic anodization. However, the pore walls are thinner in the case of galvanostatic anodization than in potentiostatic anodization. The SEM picture shows pores of median diameter 45nm approximately, but there is also a large variation in pore sizes.
Figure 4.13 Aluminum foil (~2µm thick) was anodized in 0.3M oxalic acid for 25 minutes with pore opening for 3 minutes followed by reanodization for 5 minutes. Potentiostatic anodization with a constant voltage of 40V shows through and through pores. The SEM image shows pores of 45nm median diameter approximately with variation in sizes in different pores. However this difference in pore size is less than the film in figure 4.11.

Figure 4.14 2µm thick aluminum foil was galvanostatically anodized with a constant current of 40mA, for duration of 25 minutes and pore opening of 3 minutes and 5 minute reanodization time, shows non-uniform pore formation. Some pores are not fully formed and some are over-etched. Large voids can be seen throughout the film.
3. Formation of Porous Alumina on ITO Substrate

For each experimental condition, the SEM figures are shown in the left while the corresponding current density – time curve (j-t) curve is shown in the right. For all the solutions, current density exhibits fluctuations when done at room temperature; however current density exhibits a stable stage and a fluctuating stage when anodized at lower temperatures [35]. As the anodization goes down, the Al-ITO interface, gas evolution, and sparking phenomena were observed. Meanwhile, the appearance of the specimens gradually changes from opaque to white in color, indicating the formation of aluminum anodization. The current density value depends not only on the anodizing conditions, i.e., applied potentials, acid solutions, and temperatures, but also on the conductivity of the substrate.

It is noticeable here that the surface morphologies of the anodic alumina films on ITO are significantly different from those obtained by anodization of aluminum foil or tape. As seen from the SEM images, in some cases no pores are observed but only film degradation; however in some cases we see the formation of porous films. These porous films however, are not likely to reach the Al-ITO interface, and the film morphology is not smooth and cracks can be seen on the alumina surface. The probable causes for the poor formation of porous films on ITO are poor adhesion between ITO and vacuum-evaporated aluminum as well as the need for a thicker aluminum layer because a long period of anodization is necessary in order to remove the deformation layer which formed on the surface of the alumina during mechanical finishing.

Aluminum evaporated on ITO/glass substrate was anodized in different molarities of oxalic acid and sulfuric acid. The applied voltages were expected to be lower with sulfuric acid as the electrolyte than with oxalic acid, because of higher dissolvability of aluminum in sulfuric acid than in oxalic acid. Aluminum on ITO was initially anodized by 1 step anodization as the samples in figures 4.15 (device # 110403_2), 4.19(device # 110703_1), 4.20 (device # 111003_1), 4.21 (device # 120503_1) and 4.24 (device #
120703_2). Only the sample in figure 4.20 (device # 111003_1) showed porous film growth although with large voids. However the procedure could not produce repeated similar results. The subsequent samples were also tried with 2 step anodization process as it is generally observed with aluminum films that reanodization leads to more ordered pore formation. Thus the samples in figures 4.16(device # 111103_1), 4.17(device # 111303_1), 4.20(device # 111303_3) were anodized in 10% sulfuric acid at 15 V for varying temperatures with 2 step anodization process. The temperatures were lowered to reduce the mobility of the ions in the solution thereby providing more stable current with fewer transients. The samples in figures 4.22(device # 120603_1) and 4.23(device # 120603_3) were anodized by 2 step anodization process to try to replicate the sample in figure 4.20(device # 111003_1). The sample in figure 4.25(device #030504_1) in 3% oxalic acid solution was anodized at 2°C. However only the sample in figure 4.25(device #030504_1) showed the initiation of pore formation with less surface damage.

**Figure 4.15** A 1µm thick aluminum layer deposited on ITO was anodized in 10% sulfuric acid at 15 V for duration of 8 minutes and pore opening of 1 minute at room temperature. Pores are observed along with severe cracking of the alumina surface. Pores are about 20nm in diameter.
Figure 4.16 A 1µm thick aluminum layer deposited on ITO was anodized in 10% sulfuric acid at 15V for duration of 2 minutes followed by pore opening for 1 and ½ minutes followed by reanodization for 3 minutes at 20°C. From the SEM image, we can conclude that during the formation of alumina, the film degrades and although pits are beginning to form on the surface, no formation of pores is possible.

Figure 4.17 A 1µm thick aluminum layer deposited on ITO was anodized in 10% sulfuric acid at 15V for duration of 2 minutes followed by pore opening for 1 and ½ minutes followed by reanodization for 4 minutes at 10°C. The experimental conditions are similar to the figure 4.16, but anodization was done at a lower temperature of 10°C.
The films as seen from the SEM images in figure 4.17a, show the formation of pores of 25nm in diameter approximately. The cracking on the surface of alumina is also seen.

**Figure 4.18** A 1µm thick aluminum layer deposited on ITO was anodized in 10% sulfuric acid at 15V for duration of 2 minutes followed by pore opening for 1 and ½ minutes followed by reanodization for 4 minutes at 8°C. The film was anodized at the same conditions as the film shown in figure 4.17, at 8°C. From the SEM image in figure 4.18a, porous alumina with pore diameter of 25nm is observed as well as better film surface morphology.

**Figure 4.19** A 2µm thick aluminum layer deposited on ITO was anodized in 0.2M oxalic acid at 20V for duration of 20 minutes followed by pore opening for 2 minutes at room temperature. The film degrades to alumina without pores.
Figure 4.20 A 2µm thick aluminum layer deposited on ITO was anodized in 0.3M Oxalic Acid at 20V for duration of 20 minutes and pore opening of 2 minutes. The pores’ diameters vary from 25nm to 40nm approximately. The film was observed to have regions of uniform pores along with isolated regions of large voids.

Figure 4.21 An 800nm thick aluminum layer deposited on ITO was anodized in 0.3M oxalic acid at 30V for duration of 10 minutes followed by pore opening for 2 minutes at room temperature. The film cracks with multiple fissures at the initiation of pore formation.
Figure 4.22 An 800nm thick aluminum layer deposited on ITO was anodized in 0.3M oxalic acid at 31V for duration of 6 minutes followed by pore opening for 1 and ½ minutes, followed by reanodization for 5 and ½ minutes at room temperature. In this case 2 step anodization was performed with the hope that it would yield better results, as is generally the case with anodization of aluminum tape or foil, however we do not see pore formation, although fewer cracks were observed.

Figure 4.23 An 800nm thick aluminum layer deposited on ITO was anodized in 0.3M oxalic acid at 36V for duration of 6 and ½ minutes followed by pore opening for 1 and ½ minutes, followed by reanodization for ½ minute at room temperature. This 2 step
anodization leads to pore formation, but non-uniformity of film along with regions of cracks was observed.

**Figure 4.24** An 800nm thick aluminum layer deposited on ITO was anodized in 0.3M oxalic acid at 35V for duration of 15 minutes at room temperature. Alumina with fewer cracks but without pore formation is observed.

**Figure 4.25** A 2µm thick aluminum deposited on ITO was anodized in 3% oxalic acid at 40V for a duration of 2 minutes followed by pore opening for 3 and ½ minutes, followed by reanodization for 24 ½ minutes at 2°C. From the SEM image the initiation of pore formation can be observed. While there is a need to remove the deformation layer on the
surface of alumina, the current density – time plot has less fluctuating stage and hence further improvement can be made with this condition.

4. Electrodeposition of CdS

Cadmium Sulfide was electrodeposited in the anodized alumina foil. The electrodeposition of CdS in the foil was attempted in a dc medium as well as by pulse deposition. CdS was electrodeposited into the alumina pores by an application of 10V d.c. between the ITO/alumina foil working electrode and platinum counter electrode. ITO and alumina foil were held by a single clip at the top to form the working electrode in the setup. The samples in figures 4.26(device # 122203_1) and 4.27(device # 122403_1) illustrate this setup. The sample in figure 4.26(device # 122203_1) shows CdS particles into the pores of the alumina membrane with any CdS particles on the alumina surface, however the CdS particles do not completely fill the pores. The sample in figure 4.27(device # 122403_1) has significantly overdeposited CdS particles leading to deposition on the walls of porous alumina and in the pores. In the samples in figures 4.28(device # 061204_1) and 4.29(device # 061604_1) the working electrode setup was modified with silver paste and epoxy between ITO and porous alumina respectively. However the deposition was not uniform in either case. Subsequently pulse deposition was carried on the sample in figure 4.30(device # 071504_1) with a high of 2.5V and low pulse of 2V for 15 cycles of 40 seconds each. From the SEM image in figure 4.30a, it is observed the CdS particles filled the alumina pores with a little overdeposition.
Figure 4.26 Cadmium Sulfide was electrodeposited in the anodized aluminum foil. A 10V dc voltage was applied between the ITO/alumina foil working electrode and platinum counter electrode. The process was carried out for 8 minutes. The working electrode consisted of ITO and anodized alumina foil held together only by the contact clip. It can be concluded from the SEM image that CdS deposited into some of the pores.

Figure 4.27 Electrodeposition of Cadmium Sulfide in the anodized aluminum foil at 10V applied dc voltage between the ITO/alumina foil working electrode and platinum counter electrode was performed. The process was carried out for 30 minutes. The working electrode of ITO and anodized alumina foil held together only by the contact clip. The
SEM image shows the over deposition of CdS in the pores. It is likely that CdS over deposited due to long duration of applied field as well non-uniformity of applied field.

**Figure 4.28** Cadmium Sulfide was electrodeposited in the anodized aluminum foil. A 10V dc voltage was applied between the ITO/alumina foil working electrode and platinum counter electrode. The process was carried out for 16 minutes. The working electrode consisted of ITO and anodized alumina foil with silver paste between them. However silver paste could not hold ITO and the anodized alumina foil together and the Electrodeposition was not uniform.

**Figure 4.29** Electrodeposition of Cadmium Sulfide in the anodized aluminum foil at 10V applied dc voltage between the ITO/alumina foil working electrode and platinum counter
electrode was performed. The process was carried out for 20 minutes. The working electrode of ITO and anodized alumina foil with metal epoxy to hold them together. From the SEM image we can conclude that CdS deposited only on the outer walls on the anodized alumina foil. The possible cause would be low conductivity of metal epoxy.

**Figure 4.30:** CdS was electrodeposited into the anodized alumina foil by pulse deposition method. Pulses of a high of 2.5V and low of 2V were applied between ITO/alumina foil with thermal joint compound as working electrode and platinum as the counter electrode for 15 cycles. As seen from the current time plot, the current is stable and throughout the application of high or low pulse indicating more uniform deposition. From the SEM images it can concluded that CdS particles completely filled the pores, but were slightly over deposited.

**a. Electrical Characterization of CdS**

ITO was sputtered on one side of the CdS deposited aluminum foil and (a) gold and (b) copper was evaporated in 0.07 cm² area.
Gold was thermally evaporated as a top contact on the ITO sputtered CdS/ alumina foil. The current – voltage curve in figure 4.31a, shows the behavior of this device. A high current was observed varying linearly with the applied voltage. Figure 4.31b, shows the behavior of copper evaporated on the ITO sputtered CdS/ alumina foil. The current – voltage relationship is similar to a diode with high series resistance.

**b. XRD Characterization of CdS**

The CdS deposited inside the porous alumina membrane was characterized by X-ray diffraction to determine the orientation of electrodeposited CdS. The X-ray diffraction pattern of the electrodeposited CdS prepared by electrodeposition showed peaks at 2θ positions of 25.16°, 26.8°, 28.44° and 37.12° corresponding to the planes (100), (002), (101) and (102) respectively. Thus, the XRD pattern indicated a hexagonal phase for CdS according to the 10-0454 JCPDS.
**Figure 4.32** X-ray diffraction pattern of electrodeposited CdS in porous alumina
Chapter 5. Discussion

1. Current Density vs. Varying Applied Voltage

![Current density vs Applied Voltage](image)

**Figure 5.1** Changes in steady-state current density of anodic films with different applied voltage in 0.3M Oxalic Acid. Anodizing was carried out at constant voltage.

Figure 5.1 shows the changes in steady-state current density of anodic alumina films with applied voltage. Anodizing was performed at a constant voltage for 25 minutes followed by pore opening of 3 minutes and reanodization of 5 minutes. The steady state current was generally reached after around 10 minutes of anodization. It is caused by the low dissolving ability of the oxalic acid at room temperature. Current density increased rapidly for three types of electrolytes when the voltage increased to a value close to the individual self-ordering voltage, *i.e.*, oxalic acid at 40 V. From the figure 5.1 it can be clearly seen that there is a big jump in current density when the applied voltage was increased from 30V to 40V, which is the formation voltage in the case of oxalic acid. The self-ordering voltage is strongly dependent on the pH of each electrolyte, namely, the oxide dissolution ability. At a voltage higher than the individually specified self-ordering voltage, an extremely high current was observed in the electrolyte. Thus, it is apparent that self-ordering occurs at a voltage just under the critical voltage which induces moderately high current and leads to uniform film growth.
2. Current density for Different Films/Substrates for Similar Applied Voltage

<table>
<thead>
<tr>
<th>Film/Substrate</th>
<th>Applied Voltage (Volts)</th>
<th>Current density (mA/sqcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Tape</td>
<td>40</td>
<td>3.72</td>
</tr>
<tr>
<td>25µm thick</td>
<td>40</td>
<td>17.05</td>
</tr>
</tbody>
</table>

Table 5.1 Current density for same applied voltage for anodization in 0.3M Oxalic Acid at room temperature.

Table 5.1 lists the steady state current density for the same applied voltage of 40V on aluminum tape and aluminum foil. The observed current density is much higher for the applied voltage on aluminum foil of thickness 4µm approximately than that is observed in the case of aluminum tape of thickness 25µm approximately. Also the current density is much more uniform, with less transient variation in the case of aluminum tape than in the case of aluminum foil. The low current density combined with a very stable current throughout the anodization process with aluminum tape would lead to a more ordered pore formation with better surface morphology than with aluminum foil, where higher current density would lead to faster anodization and hence comparatively more random pore growth. The SEM images in figures 4.2 and 4.5 seem to confirm the above conclusion. However, it should be noted that too low a current would lead to no pore formation but only oxidation.

3. Current Density vs. Film Thickness for Anodized Aluminum Foil

<table>
<thead>
<tr>
<th>Film Thickness (µm)</th>
<th>Applied voltage (Volts)</th>
<th>Current density (mA/sqcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>40</td>
<td>13.95</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>18.60</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>17.05</td>
</tr>
</tbody>
</table>

Table 5.2 Current density for same applied voltage for anodization in 0.3M Oxalic Acid for different thickness of aluminum foil at room temperature
Table 5.2 lists the steady state current density for an applied voltage of 40V on aluminum foils of varying thickness. It would have been expected that the current density would increase with decreasing aluminum thickness due to decreased overall resistance of the film; however this is not practically observed. While the current density of 2µm is higher than that of aluminum foil of 4µm thick; the current density of 1.5µm thick aluminum foil is lower than the other two. It is postulated that the 1.5µm thick aluminum foil has less smooth surface morphology before anodization, with possible presence of surface oxide which could explain the lower current densities. However as observed from the SEM images the current density in all the different aluminum foils were sufficient for anodization.

Current densities in the case of aluminum evaporated on ITO/glass substrate were high for the applied voltages. However an additional reason for non-formation of ordered porous alumina on ITO/glass substrate could be poorer adhesion between thermally evaporated aluminum and ITO which requires more surface polishing. A smoother ITO surface could lead to smoother aluminum film which in turn could potentially lead to the formation of porous alumina when anodized in different electrolytes.

4. Change in the Porosity of Anodic Alumina with Increasing Formation Voltage

Figure 5.2 Changes in average porosity of anodic films with different applied voltage in 0.3M Oxalic Acid. Anodization was carried out at constant voltage.
Porosity of a film is defined as the total volume of pores divided by the volume of the oxide. The porosity can also be expressed as the total area of the pores per unit surface area of the anodized specimen, since the average pore radius scarcely changes with the depth of the pores; the depth of the pores being almost equal to the total film thickness. Thus porosity can be estimated by scanning electron microscopy for films by counting the number of pores per cm$^2$ and measuring the average pore diameter. Figure 4 compares the average estimated porosity of 4$\mu$m thick aluminum foil for different applied voltages of anodization in 0.3M oxalic acid at room temperature. The observed porosity decreases with increasing applied voltage, which is consistent with the results in literature. Thus while current density increased with increasing applied voltage, the average porosity showed a reverse trend. Thus samples anodized at 20V had higher porosity than samples anodized at 50V. However porosity is not an indicator of orderliness of pores, which are observed to be most ordered at 40V as observed by comparing the SEM images in figures 4.5, 4.7, 4.8 and 4.9. Thus while pore size seems to have increased with increasing applied voltage, the number of pores as well as interpore distance also increased with increasing applied voltage. The porosity in each case was estimated from the SEM images corresponding to each condition.

5. Change in Porosity of Anodic Alumina with Increasing Reanodization Time

![Porosity Vs Varying Reanodization Time at a constant applied voltage of 40V](image)

Figure 5.3 Changes in average porosity of anodic films with different reanodization time at a constant applied voltage of 40V in 0.3M Oxalic Acid.
Figure 5.3 compares the changes in average porosity of anodized alumina films with varying reanodization time at a constant applied anodization voltage of 40V in 0.3M Oxalic Acid. The comparison at 40V is useful as it is the self-ordering voltage for anodized alumina in oxalic acid. From the figure 5.3 it can be observed that the average porosity increases with increasing reanodization time. Thus the porosity of aluminum foil of 4µm average thickness anodized at 40V for a duration of 25 minutes and reanodized for a duration of 10 minutes following a pore opening of 3 minutes is considerably higher than the porosity of aluminum foil of same thickness anodized at 40V for a duration of 25 minutes, pore opening of 3 minutes and reanodized for 2.5 minutes. However as is the case of increasing applied voltages, the increasing porosity is not a measure of orderliness of anodized film for different reanodization times. The porosity is however an indicator of how pore formations is affected by varying reanodization time. Porosity was estimated from the corresponding SEM images.

6. Porosity at Constant Voltage for Different Aluminum Films

<table>
<thead>
<tr>
<th>Film</th>
<th>Applied Voltage (Volts)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Tape 25µm thick</td>
<td>40</td>
<td>72.72</td>
</tr>
<tr>
<td>Aluminum Foil 4µm thick</td>
<td>40</td>
<td>51.24</td>
</tr>
</tbody>
</table>

Table 5.3 Average porosity for same applied voltage for anodization in 0.3M Oxalic Acid at room temperature.

Table 5.3 compares the average observed porosity for the same applied voltage of 40V in Oxalic Acid with aluminum tape of thickness 25µm approximately and aluminum foil of 4µm thickness approximately. It is observed from table 5.3 that the thicker aluminum tape has considerably higher porosity than the thinner aluminum foil. While the pore density is higher in aluminum foil than the pore density of aluminum tape the higher pore size in case of aluminum tape (75nm pore diameter) than the pore size in case of
aluminum foil (45nm pore diameter), results in higher porosity. It is likely that the higher anodization time in the case of aluminum tape would play a major role in affecting the porosity of the anodized alumina from aluminum tape. It was possible to anodize aluminum tape longer because of its higher thickness, resulting in higher porosity as well as more orderliness in anodized alumina from aluminum tape than from anodized alumina from aluminum foil. The average porosity was estimated from the corresponding SEM images.

7. Porosity at Constant Voltage for Different Thickness of Aluminum Foil

<table>
<thead>
<tr>
<th>Film Thickness (µm)</th>
<th>Applied Voltage (Volts)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>40</td>
<td>68.17</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>66.92</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>51.24</td>
</tr>
</tbody>
</table>

Table 5.4 Average porosity for same applied voltage for anodization in 0.3M Oxalic Acid at room temperature with varying aluminum foil thickness.

Table 5.4 lists the average observed porosity of aluminum foil of varying thickness at the same applied voltage of 40V in 0.3M Oxalic Acid at room temperature. It is seen from table 5.4 that the thinnest aluminum foil of thickness of 1.5µm has the highest observed average porosity, and the thickest aluminum foil of thickness of 4µm with the aluminum foil of intermediate thickness of 2µm in the middle of the table. While the pore sizes are almost constant for the aluminum foil of different thickness, the pore density varies for each aluminum foil of different thickness. However as observed from the SEM images in figures 5.5, 5.11 and 5.13, the pores are most ordered and of similar dimensions in the case of aluminum foil of 4µm thickness. The average porosity was estimated from the corresponding SEM images.
8. Porosity at Constant Foil Thickness for Potentiostatic/ Galvanostatic Anodization

<table>
<thead>
<tr>
<th>Film thickness (µm)</th>
<th>Applied voltage/ steady state voltage (Volts)</th>
<th>Applied current/ steady state current (mA/sqcm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>40</td>
<td>13.95</td>
<td>68.17</td>
</tr>
<tr>
<td>1.5</td>
<td>36</td>
<td>12.40</td>
<td>50.27</td>
</tr>
</tbody>
</table>

Table 5.5 Average observed porosity for the aluminum foils of same thickness for anodization in 0.3M oxalic acid with different anodization procedures.

Anodization in an electrolyte can be done in constant voltage mode (potentiostatic) or in constant current mode (galvanostatic). While potentiostatic anodization is more commonly observed, galvanostatic anodization has the advantage that there is less film thickening. As observed from table 5.5, the porosity of 1.5µm thick aluminum foil anodized potentiostatically is higher than the 1.5µm thick aluminum foil anodized galvanostatically. Thus while the average pore size is the same in both cases and the pore walls are thinner when anodized galvanostatically than constant voltage anodization, the pore density is greater in the case of potentiostatic anodization. The average porosity was estimated from the corresponding SEM images.

The porosity of aluminum foil of 2µm thickness of different anodization procedures could not be compared because the film developed voids while being anodized galvanostatically. The porosity of anodized alumina on ITO/glass substrate was estimated to be 10.47% in the case of anodization of 2µm thick aluminum layer on ITO/glass substrate anodized at 20V in 0.3M oxalic acid for duration of 20 minutes followed by pore opening of 2 minutes. The porosity of other samples on ITO/glass substrate could not be calculated because the films either did not have pore formations or had shallow pore formation.
<table>
<thead>
<tr>
<th>Film/Substrate</th>
<th>Solution</th>
<th>Voltage (Volts)</th>
<th>Current density (mA/cm²)</th>
<th>Anodization time, pore opening</th>
<th>Temperature (°C)</th>
<th>Porosity (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Tape</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>3.72</td>
<td>40, 2</td>
<td>22</td>
<td>72.72</td>
<td>The film shows 75 nm uniform pore openings.</td>
</tr>
<tr>
<td>Aluminum Tape</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>3.72</td>
<td>50, 2</td>
<td>22</td>
<td>72.72</td>
<td>The film shows 75 nm pore openings with ruptured pore walls at some places due to over-etching.</td>
</tr>
<tr>
<td>Al foil 4µm</td>
<td>0.3M Oxalic Acid</td>
<td>20</td>
<td>1.55</td>
<td>25, 3, 5</td>
<td>22</td>
<td>70.28</td>
<td>Pores of diameter 25nm approximately; but the film is not very uniform</td>
</tr>
<tr>
<td>Al foil 4µm</td>
<td>0.3M Oxalic Acid</td>
<td>30</td>
<td>6.51</td>
<td>25, 3, 5</td>
<td>22</td>
<td>58.56</td>
<td>Pores of diameter 25nm approximately, many pore walls have collapsed, giving the appearance of larger pores</td>
</tr>
<tr>
<td>Al foil 4µm</td>
<td>0.3M Oxalic Acid</td>
<td>50</td>
<td>26.97</td>
<td>25, 3, 5</td>
<td>22</td>
<td>30.45</td>
<td>Pores of diameter 45nm approximately can be seen, but the structure is not well-ordered</td>
</tr>
<tr>
<td>Al foil 4µm</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>17.05</td>
<td>25, 3, 2.5</td>
<td>22</td>
<td>34.13</td>
<td>Pores of diameter 45nm approximately can be seen, but not very ordered</td>
</tr>
<tr>
<td>Al foil 4µm</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>17.05</td>
<td>25, 3, 5</td>
<td>22</td>
<td>51.24</td>
<td>Pores of 45nm diameter approximately are seen</td>
</tr>
<tr>
<td>Al foil 4µm</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>17.05</td>
<td>25, 3, 7.5</td>
<td>22</td>
<td>52.06</td>
<td>Pores of diameter 45nm approximately can be seen, with thinner walls</td>
</tr>
<tr>
<td>Al foil 4µm</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>17.05</td>
<td>25, 3, 10</td>
<td>22</td>
<td>69.91</td>
<td>Pores of diameter 45nm approximately can be seen, with more thinner walls and a few broken pieces</td>
</tr>
<tr>
<td>Material</td>
<td>Acid</td>
<td>pH</td>
<td>Temperature</td>
<td>Current Density</td>
<td>Thickness</td>
<td>Pore Size</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------</td>
<td>-----</td>
<td>-------------</td>
<td>-----------------</td>
<td>-----------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>Al foil 4µm</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>17.05</td>
<td>22</td>
<td>42.72</td>
<td>Pores of diameter 45nm approximately.</td>
<td></td>
</tr>
<tr>
<td>Al foil 1.5µm</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>13.95</td>
<td>22</td>
<td>68.17</td>
<td>Big variation in pore size, can be approximated to 45nm.</td>
<td></td>
</tr>
<tr>
<td>Al foil 1.5µm</td>
<td>0.3M Oxalic Acid</td>
<td>36</td>
<td>12.40</td>
<td>22</td>
<td>50.27</td>
<td>Galvanostatic anodization. Pore size of 45nm approximately, a thin barrier layer is present.</td>
<td></td>
</tr>
<tr>
<td>Al foil 2µm</td>
<td>0.3M Oxalic Acid</td>
<td>40</td>
<td>18.60</td>
<td>22</td>
<td>66.92</td>
<td>Big variation in pore size, can be approximated to 45nm.</td>
<td></td>
</tr>
<tr>
<td>Al foil 2µm</td>
<td>0.3M Oxalic Acid</td>
<td>31</td>
<td>12.40</td>
<td>22</td>
<td>Not Available</td>
<td>Galvanostatic anodization. Pores not formed, large voids can be seen throughout the film</td>
<td></td>
</tr>
<tr>
<td>1µm Al on ITO</td>
<td>10% Sulfuric Acid</td>
<td>15</td>
<td>12.40</td>
<td>22°C</td>
<td>Not Available</td>
<td>Initiation of pores with severe cracking</td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>Material</td>
<td>Alkali</td>
<td>Voltage</td>
<td>Temperature</td>
<td>Availability</td>
<td>Remarks</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>----------</td>
<td>--------</td>
<td>---------</td>
<td>-------------</td>
<td>--------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>1µm Al on ITO</td>
<td>10% Sulfuric Acid</td>
<td>15</td>
<td>10.54</td>
<td>20°C</td>
<td>Not available</td>
<td>The film degrades and although pits are beginning to form on the surface, there is no formation of pores.</td>
<td></td>
</tr>
<tr>
<td>1µm Al on ITO</td>
<td>10% Sulfuric Acid</td>
<td>15</td>
<td>6.51</td>
<td>10°C</td>
<td>Not available</td>
<td>The formation of pores of 25nm in diameter approximately, along with the cracking on the surface of alumina is seen.</td>
<td></td>
</tr>
<tr>
<td>1µm Al on ITO</td>
<td>10% Sulfuric Acid</td>
<td>15</td>
<td>5.58</td>
<td>8°C</td>
<td>Not available</td>
<td>Shallow porous alumina with pore diameter of 25nm is observed, however film surface is not smooth.</td>
<td></td>
</tr>
<tr>
<td>2µm Al on ITO</td>
<td>0.2M Oxalic Acid</td>
<td>20</td>
<td>10.54</td>
<td>22°C</td>
<td>Not available</td>
<td>The film degrades to alumina without pores.</td>
<td></td>
</tr>
<tr>
<td>Film Thickness</td>
<td>Al Concentration</td>
<td>Time (h)</td>
<td>Oxalic Acid Concentration</td>
<td>Temperature (°C)</td>
<td>pH</td>
<td>Result</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------</td>
<td>----------</td>
<td>---------------------------</td>
<td>------------------</td>
<td>----</td>
<td>------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>2µm Al on ITO</td>
<td>0.3M Oxalic Acid</td>
<td>20</td>
<td>10.54</td>
<td>22°C</td>
<td>10.47</td>
<td>The film was observed to have regions of uniform pores along with isolated regions of large voids.</td>
<td></td>
</tr>
<tr>
<td>800nm Al on ITO</td>
<td>0.3M Oxalic Acid</td>
<td>30</td>
<td>13.02</td>
<td>22°C</td>
<td>Not available</td>
<td>No pore formation, with multiple fissures was observed.</td>
<td></td>
</tr>
<tr>
<td>800nm Al on ITO</td>
<td>0.3M Oxalic Acid</td>
<td>31</td>
<td>12.40</td>
<td>22°C</td>
<td>Not available</td>
<td>No pore formation, although fewer cracks were observed.</td>
<td></td>
</tr>
<tr>
<td>800nm Al on ITO</td>
<td>0.3M Oxalic Acid</td>
<td>36</td>
<td>13.64</td>
<td>22°C</td>
<td>Not available</td>
<td>Pore formation, but non-uniformity of film along with regions of cracks was observed.</td>
<td></td>
</tr>
<tr>
<td>800nm Al on ITO</td>
<td>0.3M Oxalic Acid</td>
<td>35</td>
<td>13.02</td>
<td>22°C</td>
<td>Not available</td>
<td>Alumina with fewer cracks but without pore formation is observed.</td>
<td></td>
</tr>
<tr>
<td>2µm Al on ITO</td>
<td>3% Oxalic Acid</td>
<td>40</td>
<td>1.86</td>
<td>2, 3 ½, 24 ½</td>
<td>2°C</td>
<td>Not available</td>
<td>Initiation of pores is observed along with deformation layer.</td>
</tr>
</tbody>
</table>

**Table 5.6** List of anodization conditions

Table 5.6 lists the different anodization conditions on aluminum tape, aluminum foil and aluminum evaporated on ITO/glass substrate, in various electrolytes for different anodization time at different temperatures. It describes the observed conditions for each case. Thus while more uniform pores are obtained with the thicker aluminum tape; the anodization of aluminum evaporated on ITO/glass has proven to be less successful.

9. **Series Resistance (R_s)**

The J-V characteristics of an abrupt p-n junction devices are usually governed by the “ideal diode equation” (equation 5.1) in an ideal case.

\[
J = J_o \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right]
\]

where \( J_o \) = reverse saturation current density,
q = charge of an electron = 1.6 x 10^{-19} C.
k = Boltzman constant = 1.38 x 10^{-23} J.K^{-1} and

\( T = \) Absolute Temperature in degrees Kelvin.

According to equation 6.1 for an ideal diode,

1. The diffusion (exponential part) and drift (-\( J_o \)) currents balance at zero bias (V=0), canceling each other and resulting in an absence of net current flow.
2. In forward bias, the barrier decreases, diffusion current increases exponentially and the drift current is unaltered.
3. In reverse bias the barrier increases, diffusion current is negligible and drift current is unaltered [39].
However, in some real-world cases, the ideal diode equation may not be very applicable due to the effects of series resistance, leakage current and other factors. In these cases, equation 5.1 should be modified accordingly.

For Schottky diodes, the J-V characteristics becomes linear at high voltages (and high currents) due to the series resistance. Series resistance is the resistance caused by the quasi neutral regions and the contacts made to the device. When a device shows series resistance then the potential drop is not just due to the junction but also due to $R_s$. This potential drop due to $R_s$ needs to be separated from the applied potential so that the J-V characteristics can be corrected and the current component only due to the diode behavior is extracted. Equation 5.1 would then be modified to equation 5.2

$$J = J_o \left[ \exp \left( \frac{q(V - JR_s)}{nkT} \right) - 1 \right]$$

Where $R_s$ is the series resistance and therefore the potential drop across junction is calculated by $V - JR_s$. $R_s$ can then be calculated mathematically from the J-V characteristics.

On differentiating equation 5.2 we get,

$$1 = J_o \frac{q}{nkT} \left( \frac{dV}{dJ} - R_s \right) \exp \left[ \frac{q(V - JR_s)}{nkT} \right]$$

So,

$$\frac{dV}{dJ} = \frac{nkT}{qJ_o} \exp \left[ \frac{-q}{nkT} (V - JR_s) \right] + R_s$$

Again, from equation 5.2 and ignoring a $J_o$ term, we can rewrite equation 6.3 as,

$$\frac{dV}{dJ} = \frac{nkT}{qJ} + R_s$$

When the applied bias is high, the current through the device would also be large. The first term in equation 5.4 would be negligible in this case. So at a higher bias (large $J$) the series resistance can be estimated with the slope of the J-V curve [40]. The series resistance values calculated for ITO/CdS/Cu junction inside porous alumina foil was 15.238 kΩ/cm$^2$. The J-V characteristics corrected for series resistance are depicted in figure 5.4. The ideality factor was estimated to be 6.85837 and the saturation current was 2.3525e-008 Amps with an error fit factor of 6.0239e-012.
Figure 5.4 J-V curve fitted for series resistance
Chapter 6. Conclusion

The results of a systematic study of anodization of different aluminum films in electrolytic solution are presented. From the current density-time characteristics monitored during the anodization process, and the SEM images of the films the conditions of the various films were determined. The current density increases linearly with applied voltage, porosity on the other hand decreases with increasing applied voltage. The thickness of the original films also has a direct bearing on the morphology of the obtained films. Comparing the films obtained by anodizing alumina at different applied voltages, it is clear that the best films are obtained when the anodization takes place at an applied voltage that is close to self-forming voltage for the particular electrolyte, which is 40V in the case of oxalic acid. The reanodization time also had a significant on the final quality of the films obtained. The best quality porous alumina films were obtained when the film was reanodized for duration of 5 minutes. Anodization of films on ITO/Glass substrate was also attempted and with a few successes further work needs to be done to refine this process.

By observing the characteristics of the porous alumina films, it can be concluded that

1. Pore initiation in anodic alumina films forming at constant voltage are related to the substrate substructure and the subsequent concentration of current into the regions.
2. The pore diameter is dependent on the applied voltage.
3. The pore diameter and the film morphology are proportional to the self-forming voltage.
4. The film morphology is a function of the reanodization time.
5. Pore opening process is essential for reducing the barrier layer thickness.
6. Increasing or decreasing of the applied voltage during anodization leads to redistribution of pore populations, requiring pore merging or termination and pore initiations.
7. The self-forming voltage varies with the electrolyte being used. Electrolytes which have higher dissolution ability of aluminum have lower self-forming voltage.

As an application to the above fabricated anodized alumina, CdS was electrodeposited into the pores by various techniques. Both d.c. as well as pulse deposition techniques were used. In some cases, selective electrodeposition of CdS arrays in the porous alumina matrix was achieved. The XRD of the films confirmed that the electrodeposited CdS had a hexagonal phase with peak positions corresponding to (100), (002), (101) and (102) planes. Different methods of making contact to the anodized alumina were also used. Electrical characterization of some of the electrodeposited films was done with ITO as the back contact and Gold/Copper as the top contact. In case of the films with copper contacts, a diode like behavior with high series resistance of 15.238 kΩ/cm² was observed. Further analysis can be done on electrodeposited CdS/Cu interface to forms a better Schottky diode. These results can be compared with the present work to have a better insight into the properties of electrodeposited CdS. This work can also be further continued by making electrodeposited CdS/CIS solar cells inside the porous alumina matrix.
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