The kinetics for film growth of yttria doped zirconia are modeled considering a Wagner oxidation process. The growth kinetics are examined as a function of reaction temperature, yttria content in the film, as well as the oxygen partial pressure gradient across the film. Calculated results indicate that only at temperatures above 1300 K, and low doping levels is the growth rate governed by the diffusion of electrons. With decreasing temperature and increasing yttria content the diffusion of holes becomes increasingly important in the growth rate. These model studies are used to explain differences in observed morphologies of EVD grown films of YSZ.

1. Introduction

Electrochemical vapor deposition (EVD) is a technique for producing thin (10-50μm) gas tight layers of metal oxides upon porous substrates (1). The first step in film formation proceeds by a normal CVD type reaction.

Step 1, Pore closure:
\[ \text{MeCl}_4 + 2 \text{H}_2\text{O} \rightarrow \text{MeO}_2 + 4 \text{HCl} \]  

The substrate separates the reactant metal chlorides from a mixture of \( \text{H}_2 \) and steam. Deposits of the metal oxide forming in the pores of the substrate eventually lead to pore closure. Once pore closure is complete the reactants are no longer in direct contact. Film growth proceeds due to the large oxygen partial pressure gradient which exists across the film. Typically, on the \( \text{H}_2\text{O}/\text{H}_2 \) side the oxygen partial pressure (\( \text{Po}_2 \)) is \( 10^{-4} \) atm, whereas on the metal chloride side it is on the order of \( 10^{-16} \) atm. This large \( \text{Po}_2 \) gradient results in the diffusion of oxygen anions from the \( \text{H}_2\text{O}/\text{H}_2 \) side to the metal chloride side. The second step, scale growth, proceeds due to the reaction of oxygen anions with metal chlorides:
Step 2, Scale growth:
\[ \text{MeCl}_4 + 2 \text{O}^= \rightarrow \text{MeO}_2 + 2 \text{Cl}_2 + 4 \text{e}^- \]  \hspace{1cm} (2)

\[ 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 2 \text{H}_2 + 2 \text{O}^= \]  \hspace{1cm} (3)

Carolán et al. have modeled the dynamics of the CVD step leading to pore closure for the growth of yttria doped zirconia (2). In this work the dynamics of the second step are examined as a function of the reaction temperature, yttria content in the film, and oxygen partial pressure gradient across the film.

2. Model

The kinetics for film growth are calculated considering a Wagner oxidation process (3,4). In this case film growth is governed by solid state diffusion through the oxide. The diffusion processes which take place during EVD growth are shown schematically in Figure 1. The partial pressure of oxygen on the \text{H}_2\text{O}/\text{H}_2 \text{ side of the substrate (Po)} is determined by the equilibrium between the gases. Similarly the oxygen partial pressure on the metal chloride side (Po') is determined by the equilibrium between \text{MeCl}_4', \text{Cl}_2', \text{and MeO}_2. The large oxygen partial pressure gradient across the film results in a flux of oxygen anions (O^=) to the metal chloride side. Electroneutrality is preserved through an opposing electronic flux. At steady state the sum over the ionic (i), electronic (e') and hole (h') fluxes is given by:

\[ i = 0 = \sum_{i,e,h} Z_k J_k \]  \hspace{1cm} (4)

where \( Z_k \) is the charge on species k, and \( J_k \) the flux of species k. In Wagner oxidation the rate of scale growth is inversely proportional to the oxide thickness, \( L \) (3).

\[ \frac{dL}{dt} = K \frac{1}{L} \]  \hspace{1cm} (5)

The integrated form of equation 5 yields the parabolic rate law

\[ L^2 = 2Kt + C_0 \]  \hspace{1cm} (6)

where \( C_0 \) is a constant of integration.
Alternatively the growth rate can be expressed in terms of the ionic flux. Assuming that all anions that pass through the film react to produce electrolyte, the growth rate is given by:

$$\frac{dL}{dt} = \frac{1}{2} \frac{J}{\rho} mw$$

(7)

where $\rho$ and $mw$ are the density and molecular weight of the growing oxide. For an ionic conductor the general expression for the ionic flux is given by (4):

$$J = \frac{kT}{8e^2} \frac{1}{\langle r \rangle} \frac{d}{d\ln P_{O_2}} \left[ \int_{P_{O_2}}^{P_{O_2}'} \sigma_{el} d\ln P_{O_2} \right]$$

(8)

where $k$ is Boltzmann's constant, $T$ is absolute temperature, $e$ is the charge of an electron, and $\sigma_{el}$ the sum of the electron and hole conductivities. From equations 7 and 8 the rate constant for film growth can be derived yielding:

$$K = -\frac{1}{16} \left[ \int_{P_{O_2}}^{P_{O_2}'} [h'] D_h + \int_{P_{O_2}'}^{P_{O_2}''} [e'] D_e \right] d\ln P_{O_2}$$

(9)

where $[h']$ and $[e']$ represent the mole fraction of holes and electrons and $D_h$ and $D_e$ their respective diffusion coefficients. The pressure at which the electronic conductivity changes from n type to p type is represented by $P_{O_2}'$.

The rate constant is integrated in parts to take into account the variation in $[h']$ and $[e']$ with oxygen partial pressure. The pressure dependence of $[h']$ and $[e']$ can be understood by considering the defect reactions responsible for their formation. In YSZ, the formation of doubly charged oxygen vacancies $[V^{2+}]$ results in the formation of quasi-free electrons and the annihilation of holes. In Kröger-Vink notation these defect reactions are written as:

$$2h' + O^{2+}_O \xrightarrow{K_1} V^{2+} + \frac{1}{2} O_2(g)$$

(10)

$$O^{2+}_O \xrightarrow{K_2} V^{2+} + \frac{1}{2} O_2(g) + 2e'$$

(11)

Solving for $[h']$ and $[e']$ from the above reactions yields the equilibrium expressions:

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\[
[h'] = \frac{[V_0]^{1/2} P_0^{1/4}}{[O_0^X]^{1/2} K_1^{1/2}}
\]  

\[
[e'] = \frac{[0^X]^{1/2} K_2^{1/2}}{[V_0]^{1/2} P_0^{1/4}}
\]

Thus, the hole concentration varies with \( P_0^{1/4} \) whereas the electron concentration varies with \( P_0^{-1/4} \).

Under typical EVD growth conditions the oxygen partial pressure gradient ranges from \( 10^{-4} \) atm to \( 10^{-16} \) atm. The variation of the electronic conductivity over this pressure range is shown in Figure 2. At high \( P_0^2 \) holes dominate the electronic conductivity whereas at low \( P_0^2 \) electrons dominate the electronic conductivity. As shown in Figure 2, the log of \( P_0^r \) varies linearly with temperature. With increasing yttria content (X) this line shifts to higher oxygen partial pressures.

To obtain numerical values for \( K \) the functional dependence, \( f(X,T,P_0) \), for \( \sigma \) as well as \( D_e, D_h, K_1, K_2 \) and \( V_0 \) were calculated. The data necessary for these calculations was derived from the work of Weppner \( (5,6) \) and Honke \( (7) \). The lower limit of integration, \( P_0^2' \), was determined by the equilibrium of the \( H_2O, H_2, O_2 \) gas mixture at a given temperature. The integration limit \( P_0^2' \) was taken to vary with \( X \) and \( T \) according to the functional dependence given in Figure 2. The upper limit, \( P_0^{2''} \), is taken to be \( 10^{-16} \) atm throughout these calculations.

3. Results

The total rate constant for film growth is the sum of the electronic \( (K_e) \) and hole contributions \( (K_h) \). The effect of increasing temperature upon the relative magnitudes of \( K_e \) and \( K_h \) is shown in Figure 3. At low temperatures, \( T < 1300 \), \( K_e \) is of the same order of magnitude as \( K_h \) and both contribute of the overall growth rate. With
increasing temperatures $K_e$ rapidly becomes orders of magnitude greater than $K_h$. The contribution of holes is so small at high temperatures that film growth is rate limited by the diffusion of electrons alone.

Not only does temperature affect the relative magnitudes of $K_e$ and $K_h$ but also the mole fraction dopant (Y$_2$O$_3$) affects the film growth rate. Addition of Y$_2$O$_3$ to ZrO$_2$ results in the formation of oxygen vacancies. From the equilibrium expressions for [h'] and [e'], it is clear that with increasing $V_0$, [h'] increases and [e'] decreases. Consequently, with increasing Y$_2$O$_3$, $K_h$ increases while $K_e$ decreases (Figure 4). At very low reaction temperatures and high X the diffusion of holes dominate the film growth kinetics, $K_h > K_e$.

Under most conditions (T>1100 K and X<0.10) the overall rate constant decreases with increasing yttria content (Figure 5). The Arrhenius plot (Figure 6) yields an activation energy of 3.85 eV for the growth of 10 mole percent Y$_2$O$_3$ in ZrO$_2$. These calculations predict a relatively slow growth rate for YSZ. The average $K$ is on the order of $10^{-10}$ (cm$^2$/sec). Applying the parabolic rate law yields an average growth rate of 6 μm/hour. Similar growth rates have been observed by Isenberg et al. (1).

4. Experimental

A schematic drawing of the EVD reactor used to grow thin films of YSZ is shown in Figure 7. Films were grown on calcium stabilized zirconia. Typically, the open porosity of the substrate was 40 % having an average pore diameter of 5 μm. A 80:20 mixture of H$_2$ in steam was passed along one side of the substrate. On the other side a mixture of volatized yttrium and zirconium chlorides was passed in an argon stream. Films were grown under reduced pressure (10 torr) and temperatures between 1200-1375 K.

Scanning electron micrographs were taken with a JEOL JSM35 operating at 25 kV. Films grown under these conditions are shown in Figure 8. Two types of morphologies are observed: a somewhat faceted surface for films grown below 1300 K and a cauliflower textured surface for films grown above 1300 K. The turning point in observing one morphology over the other occurs at the same temperature in which the kinetics of film growth becomes dominated by electron diffusion. The change from a faceted surface to a cauliflower surface can be explained by a change in kinetics. A faceted surface forms when the reaction proceeds slowly through the diffusion of both electrons and holes. At temperatures above 1300 K and X< 0.10, the growth rate is determined by the diffusion of electrons. Film growth is much.
faster when limited only by electron diffusion and results in the cauliflower textured surface.

6. Conclusions

Kinetic model studies yield an average growth rate of 6 μm/hour for the EVD scale growth of yttria stabilized zirconia. The activation energy is calculated to be 3.85 eV for the growth of 10 mole percent Y₂O₃ in ZrO₂. These results are in quantitative agreement with experimental observations (1). Model studies indicate that film growth is rate limited by the diffusion of both electrons and holes. The hole contribution to the overall growth rate is greatest at low temperatures and high doping levels. At temperatures above 1300 K film growth becomes dominated by the diffusion of electrons. The change in kinetics which occurs at 1300 K can account for the different film morphologies which form at temperatures above and below 1300 K.

References

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Figure 1: Diffusion processes occurring during the EVD growth of YSZ.

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\begin{align*}
\text{H}_2\text{O}/\text{H}_2 & \quad \text{MeCl}_4 \\
V_0^- & \quad P_{O_2} \approx 10^{-4} \text{ atm} \\
O_0^x & \quad P_{O_2}'' \approx 10^{-16} \text{ atm} \\
q^+ & \quad \text{YSZ}
\end{align*}
\]

Figure 2: Dependence of the partial conductivity as a function of oxygen partial pressure.
(Data adapted from Weppner (5,6).)
Figure 3: Temperature dependence of $K_e$ and $K_h$ for $ZrO_2 + 10$ m/o $Y_2O_3$.

Figure 4: Dependence of $K_e$ and $K_h$ upon mole fraction ($X$) of $Y_2O_3$ at 1200 K.
Figure 5: Plot of the overall rate constant \( K = K_e + K_h \) versus mole fraction \( X \).

Figure 6: Arrhenius plot of overall rate constant for \( \text{ZrO}_2 + 10 \text{ m/o Y}_2\text{O}_3 \).
Figure 7: Schematic of EVD reactor used to grow thin films of YSZ.

Figure 8: Scanning electron micrographs of EVD grown films of YSZ. Left: Film grown at 1273 K for 150 min. at 10 torr (500X). Right: Film grown at 1334 K for 135 min. at 10 torr (5000X).