Interface phenomena in multilayers deposited by PECVD for encapsulation of lithium microbatteries

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Abstract. Lithium microbatteries are easily degraded in the atmosphere: these devices require permeation barrier films exhibiting very low permeation rates for water vapor and oxygen. Such barriers made of dielectric multilayers of SiO\textsubscript{x} are deposited by low frequency plasma enhanced chemical vapour deposition. During the deposition process, two consecutive SiO\textsubscript{x} layers are separated by an argon plasma treatment which creates a specific interface. The barrier properties of the multilayers were assessed using the “lithium test”, which allows the determination of transmission rates of oxygen and water vapor. Interface phenomena were studied as a function of thickness and correlated with the critical thickness.

1. Introduction

Devices sensitive to the environment require permeation barrier films whose properties depend on applications [1,2]. Whereas sensitive food products can be protected with a single polymer film, OLED displays or lithium microbatteries need a complex layer stack of inorganic materials as a permeation barrier, leading to a very low water vapor transmission rate WVTR (some 10\textsuperscript{-6} g/m\textsuperscript{2}.day) [3]. This study focuses on the barrier properties of a multilayer stack composed of SiO\textsubscript{x} films separated by an argon plasma treatment. The barrier properties were assessed using an innovative test: the “lithium test”. The role of the plasma treatment is to create a specific interface between two consecutive layers, which could impede the diffusion of oxygen or water vapor. 1 µm thick samples with a varying number of layers were measured. So the interface phenomena were assessed.

2. Experimental

2.1. Plasma enhanced chemical vapor deposition of barrier coatings

The silicon oxide films (SiO\textsubscript{x}) were deposited at room temperature and low pressure (0.5 mbar) in a low frequency plasma (lf-PECVD) reactor with low-frequency generator (100 kHz). The precursor gases SiH\textsubscript{4} and CO\textsubscript{2} were introduced through a showerhead with a ratio of 20:1. Plasma treatments were made using the 100 kHz generator at 300 W and 0.25 mbar. SiO\textsubscript{x} multilayers were characterized
by X-Ray reflectometry (XRR) and ToF-SIMS. A Tencor Flex measurement was used to measure the film stress.

2.2. Characterizations of barrier properties by the “lithium test”

2.2.1. Theory of diffusion applied to the lithium

Lithium is a material sensitive to the atmosphere. Its oxidation is very fast, leading to a net weight increase corresponding to the cumulative amount of oxidizing species that cross the coating film. The weight increase versus time is plotted in Figure 1. The curve can be decomposed into three parts: the first two correspond to a transition and a permanent state, during which gases adsorb at the surface, diffuse through the barrier film and then oxidize the lithium. In the permanent state, the transmission rate of oxygen and water vapor across the barrier coating is constant, causing the weight to evolve linearly with time: \[ \Delta \text{weight} = \alpha t + \beta, \] where the slope \( \alpha \) is the transmission rate of the film (in units \( \mu g/cm^2 \cdot hr \)). The third part of the plot is a saturation state which corresponds to the total oxidation of the lithium.

![Figure 1: Typical representation of the evolution of weight versus time for a SiO\textsubscript{x} film](image)

In the permanent state, the permeation flux of the permeate (O\textsubscript{2} or water vapor), which is akin to a diffusion flux [4], can be written as:

\[
\alpha = P \cdot \frac{p_1}{l},
\]

where \( P \) is the permeability of the system (polymer and deposited inorganic layer), \( p_1 \) the upstream pressure in the permeation chamber and \( l \) the system thickness.

2.2.2. “Lithium test” set-up

In order to test the barrier properties of the coatings, barrier films were deposited on a system of Li patterns deposited on a silicon nitride coated Si wafer, Si\textsubscript{3}N\textsubscript{4} acting as a diffusion barrier material. The pattern, deposited by evaporation, has a size of 1 cm\textsuperscript{2} and is 3.5 \( \mu m \) thick. A passivation layer of parylene-c about 5 \( \mu m \) thick covers the dot. An accurate balance measures the weight change. Barrier systems were placed in a climatic chamber at 85°C and 85% RH in order to speed up aging.

3. Results and discussion

3.1. Critical thickness
The slope $\alpha$ decreases with thickness in a manner similar to the evolution of OTR or WVTR [5]. The plot of $\alpha$ can be divided into two regions (Figure 2). The first one is the critical thickness region, below which there is no barrier effect and over which the permeation rate decreases quickly. The critical thickness of the SiO$_x$ material lies between 20 and 50 nm. The second region shows a slow decrease of $\alpha$ with thickness, the permeation rate being essentially governed by defects.

Figure 2: The two regions in the plot of the slope $\alpha$ versus thickness

3.2. Influence of plasma treatment

In order to reduce the slope $\alpha$, SiO$_x$ multilayers were studied. For multilayers deposited under the same conditions as a SiO$_x$ single layer with the same total thickness (1 µm) and without any plasma treatment, the slopes of the two curves are similar (Figure 3). However for a multilayer (10 x 100 nm) deposited using an Ar plasma treatment between two consecutive layers, the permeation rate decreases by a factor four.

Figure 3: Influence of plasma treatment for 1 µm thick SiO$_x$ multilayers

Characterizations were undertaken in order to understand the possible effects of the Ar plasma. XRR measured a local increase in SiO$_x$ density (within a depth of 20 nm) after each successive plasma treatment. It is possible that the Ar ions have sufficient energy to rearrange the surface of each layer, thus inhibiting the diffusion of gaseous molecules.

3.3. Influence of the number of interfaces
Several samples with total multilayer thicknesses of 1 µm were studied by changing the number of interfaces and their thicknesses. This demonstrated the role of interfaces. The plot of the slope $\alpha$ (Figure 4) can be decomposed into several regions and correlated with the curve of $\alpha$ versus thickness (Figure 2). When considering a low number of interfaces and a high thickness (200 nm - 1 µm) (region 1), the slope $\alpha$ decreases quickly because the thickness of each layer is far beyond the critical thickness (see region 2 of Figure 2). So the number of interfaces has little effect on further decrease of the slope. When increasing interface number (region 2), the thickness of each layer (decreasing from 200 nm to 50 nm) remains higher than the critical thickness, so that the increase of $\alpha$ with thickness is well balanced by the increasing interface number (beneficial effect of interfaces). The region 3 (thickness in the range 20-50 nm) is more complex to analyze because the large variation of $\alpha$ with thickness is overcompensated by the important role of the interfaces. With further increases of the number of interfaces (region 4), each layer (10 - 20 nm) no longer acts as a permeation barrier, so the slope of the system increases and attains the value ascribed to a single SiO$_x$ layer. Concerning the stress evaluation, $-20$ MPa were measured for a 1 µm thick SiO$_x$ layer, which is not significant.

Figure 4: Influence of number of interfaces for 1µm thick SiO$_x$ multilayers

4. Conclusion

SiO$_x$ layers deposited by low frequency PECVD have been studied as permeation barrier films. One layer is not sufficient to prevent the devices from degradation. SiO$_x$ multilayer stacks (1µm total thickness) using an argon plasma treatment between consecutive depositions significantly decreased the permeation rate, due to a possible atomic rearrangement of the interfaces. Optimization of parameter pairs (interface number – thickness) led to a minimum permeation rate, taking into account the average critical thickness and the beneficial effect of the interfaces.

References

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