A Computational Framework on Pinhole Damage in Ultrathin Barriers for Flexible Electronics Encapsulation

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***Abstract*—This study investigates pinhole defects in nanometer thin barriers such as atomic layer deposited inorganic films encapsulating flexible organic electronics. The pinhole size and densities are correlated with barrier quality in terms of water vapor transmission rates. The proposed computational framework validated with experiments enables simulation of high aspect, i.e. two hundred, and thickness, i.e. four thousand, ratios between ultrathin inorganic film - organic polymer substrate as an interim step to designate the barrier hermeticity and thus the lifetime of compliant electronics.**

Keywords— pinhole defects, finite element analysis, water vapor transmission rates, inorganic thin film barriers, flexible organic electronics encapsulation.

I. Introduction

Thin film barriers prepared with vacuum deposition methods are a promising conformal and hermetic encapsulation strategy to overcome the limited lifetime of next generation flexible organic electronics. Most organic devices are based on lightweight, thin, and compliant polymer substrates and, thus, are compatible to be wearable and implantable bioelectronic applications. Meanwhile, organic substrates are prone to moisture permeation due to the nature of their diffusion properties, degrading fast the functional layer. Such moisture sensitive substrates are encapsulated with conformal hermetic coatings yet are thin enough to maintain high mechanical compliance. The most promising technique amongst the vacuum deposition methods is atomic layer deposition (ALD), ideally known as a nearly defect-free deposition technique. The ALD grown films can produce uniformly deposited coating layers onto high aspect ratio microfabricated structures at low temperatures and thus the process also yields low residual stresses. ALD grown ultrathin metal oxides and nitrides, e.g. Al_2O_3, TiO_2, HfO_2, SiN_x, offer extremely low water vapor transmission rates (WVTRs), on the order of 10^{-4} g/m^2/day, and significantly enhance the device lifetime to over a several years. Although further enhancement towards WVTR on the order of 10^{-6} g/m^2/day and lifetime over a decade can be achieved using multilayer encapsulation and physical transfer after high temperature deposition, the presence of pinholes and defects in ALD hinder further improvement. It is vital to produce high quality single ALD layers to meet the need of chronic working implantable and wearable devices, simplify the encapsulation process, and promote cost-effective deposition. Most importantly, the lack of systematic understanding on the effect of pinhole distributions on barrier performance gives a critical challenge in inspecting quality of deposition and predicting the lifetime. In this work, we build a computational framework by using finite element method (FEM) to better understand the correlation between pinhole defects and WVTRs. We first collect experimental findings in the literature and our own testing of ALD Al_2O_3 films on polyimide substrates as an example configuration of inorganic film/organic substrate. Experimental studies [1-3] investigate the effect of pinhole sizes and their distributions on the moisture diffusion capability. Although experiments provide some insight into the relation between them, it is still formidable to understand the exact relationships and trade-offs between these factors. Hence, we build the user-friendly interface and implement it in the commercially available software ANSYS to help predict WVTR values of thin, flexible organic devices encapsulated with inorganic ultrathin films down to a few nanometers. The software can compute possible pinhole sizes and distributions from measured WVTR and vice versa. The pinhole size range is chosen in the micro (~400 μm) to nano (~300 nm) level and the behavior of WVTR changes upon pinhole distributions is investigated to help build the data of structure-property-performance relationship of encapsulation-substrate interface for moisture resistant hermetic flexible electronics.

II. Theory

A. Fick's Law for Diffusion

The moisture diffusion inside organic materials such as polymers can be defined by linear first Fick's law as

$$\mathbf{J} = -D\nabla C \qquad (1)$$

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where **J** represents diffusion flux, D (m^2/s) is diffusivity, and C (kg/m^3) is the moisture concentration of the solute. Conservation of mass solute during the diffusion process must be satisfied by

$$\nabla \bullet \mathbf{J} + \partial_t C = \Theta \tag{2}$$

in which Θ ($kg/m^3/s$) is the rate of generation of solute per unit volume and ∂_t designates partial derivative with respect to time. Thus, moisture phenomenon inside polymers can be described by combining (1) and (2):

$$\partial_t C = D\Delta C + \Theta \tag{3}$$

Equation (3) is the second Fick's law valid only for homogeneous domains. Since the concentration of solute is dependent on solvents, it may become discontinuous across the interface of different solvents. Therefore, a normalized concentration called wetness, w, was introduced by Wong *et. al.* [4] as the ratio of concentration to the saturated concentration, C_{sat} which defines the maximum moisture concentration of a material that can be absorbed per unit volume. In light of wetness, w, the second Fick's law can be rewritten as

$$C_{sat}\partial_t w = DC_{sat}\Delta w + \Theta \tag{4}$$

Hereby, (4) is valid both for homogeneous and nonhomogeneous domains. Moreover, the wetness parameter is continuous at the interfaces of a multi-material system and thus it automatically satisfies the equality principle of chemical potentials at any instant of time.

B. Water Vapor Transmission Rate (WVTR)

WVTR is the amount of water molecules permeating through a substance or material at specified conditions of temperature and relative humidity over a period of time (Fig. (1)). Hence, WVTR (weight/area/time) can be computed as diffusion flux **J**, defined in (1), at the surface of a material. In finite element (FE) computations, the nodal diffusion flux results are read at the dry surface side, and they are summed at each element after averaging with element surface area.

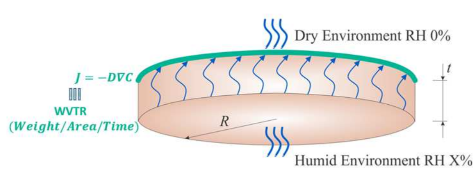

Fig. 1. The geometry and boundary conditions of 5mil Kapton HN polyimide film along with definition of water vapor transmission rate.

III. Experiments

A-127 µm thick polyimide film (Dupont Kapton HN) is used as a substrate material. It has an open surface area of 5 cm^2. The experiment is carried out at 37 ºC with RH 10%, 25% and 50% over the surface area of 5 cm^2 (Ametek Aquatran 3) following ASTM F3299. The polyimide substrate is then coated by ALD Al_2O_3 with a growth per cycle of 1.4Å at 200 ºC. A 200 cycles deposition yields 28nm thick Al_2O_3 film. Each precursor (TMA and H_2O) was utilized with nitrogen (N_2) as the purge gas.

IV. Model

The finite element model of polyimide film is generated in commercially available software, ANSYS. Since thermal and moisture diffusions have the same methodology, a three-dimensional 8 node thermal solid element, i.e. SOLID278, is utilized in computations. The thermal diffusion equation based on Fick's second law is given by

$$\rho c_v \partial_t T = k_T \Delta T + \Theta \tag{5}$$

where ρ, c_v and k_T represents the density, specific heat and thermal conductivity. In (5), the field variable is temperature, T. By comparing (4) and (5), the calibration procedure of SOLID278 element is demonstrated in Table 1. After calibrating the thermal element in ANSYS software, the listed temperature results represent the field variable wetness, w.

TABLE I. Calibration of Thermal Element for Moisture Analysis

SOLID278		
Properties	***Original***	***Modified***
Density	ρ	1
Specific Heat	c_v	C_{sat}
Thermal Conductivity	k_T	DC_{sat}

V. Numerical Results

Numerical results concern the validation of experimentally acquired WVTRs of polyimide films with and without Al_2O_3 coatings. The film has a cylindrical shape as in Fig. 1. The thickness and radius are t=127 µm and R=12.616 mm, respectively. The bottom surface is subjected to a wet condition under defined relative humidities (RH) of 10%, 25%, and 50% at constant temperature of 37 ºC and top surface is kept dry with RH 0% as in MOCON device with the help of N_2 gas.

Since wetness, w, is a non-dimensional variable, the boundary conditions (BC) are implemented as equal to one and zero to the nodes of bottom and top surfaces, respectively, in the finite element model. The diffusivity, D, values are investigated in [5] for the polyimide film applied in this study based on temperature variations and it is found to be equal to 5.37×10^{-7} cm^2/min at 37 ºC. Saturated concentration is a material property, and it depends on relative humidity of an environment and temperature. It can also be defined based on WVTR data as:

$$C_{sat} = \text{WVTR}\times t/D \tag{6}$$

The WVTR data are extrapolated from experiments carried out at different RH levels. Substituting those data into (6), the C_{sat} values are found to be 2.22, 5.987 and 11.41 kg/m^3 for 10%, 25% and 50% RH, respectively.

A. Uncoated Film

At first, the experiments are validated with FE results for the uncoated polyimide film. The steady state WVTR values saturated after 200 hours are 1.35, 3.65 and 6.95 g/m^2/day, less than 0.1% difference compared to experiments.

B. Coated Film

In FE simulations, the pinholes are defined as BCs through the bottom or wet surface of the film and they are distributed periodically with the distance between pinholes as; $l=\sqrt{\pi R^2/n}$ in which n represents the total number of pinholes on polyimide film. Fig. 2 shows such periodic distribution of pinholes by demonstrating the diffusion flux at the top surface of the film.

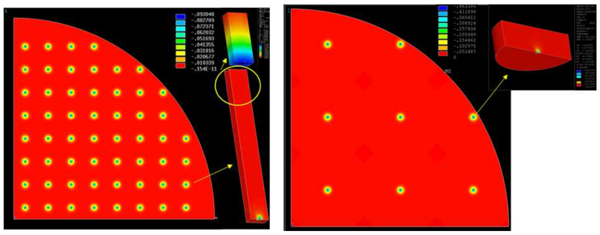

Fig. 2. Diffusion flux at the top surface for 224 pinholes with 1.38 μm size (left) and for 32 pinholes with 10.60 μm size (right).

Combinations of pinhole number and size that predict WVTR as 8×10^{-4} g/m^2/day are plotted over the range of periodically distributed pinholes, diameter from 330 nm to 282 μm and number up to 764 (Fig. 3, top). As the pinhole diameter decreases, the number of pinholes required for the equivalent WVTR increases, however, the total surface area exposed to pinhole damages dramatically decreases 10^3 times from 6×10^{-4} to 6×10^{-7} cm^2. Hence, WVTR is more sensitive to number of pinholes than size, likely due to a reduced diffusion pathway length overall. [6]

Furthermore, the variation of WVTR is investigated by changing the size of pinholes from 10 μm to 400 μm but keeping the total number of pinholes as 32 and by keeping the size of pinhole as 10 μm while altering the numbers from 4 to 428. These studies are plotted in Fig. 3 (bottom) on the left and right axes, respectively. It can be inferred that WVTR varies linearly upon the variation of sizes and numbers of pinholes on the logarithmic scale. Normally, functional layers (e.g. metal tracks) used in flexible electronics are located in between polymer substrates. Then, e.g., a few micron metal tracks with a submicron thick accumulated H_2O after 20 years under WVTR of 10^{-4} g/m^2/day (i.e. 0.73 μm) may be electrically functional. In terms of pinhole damages, ultrathin inorganic barriers restricted to the number of pinholes and the size of pinholes below 4 with 10 μm or 32 with 2.09 μm respectively, as calculated from Fig. 3 (bottom) that can satisfy the proposed barrier quality. The density of pinholes decreases as thickness and deposition temperature increase, but the increased thickness reduces mechanical flexibility (elastic limit) and high deposition temperature accelerates residual stresses. Such relationships can help design better deposition parameters of inorganic barriers. However, this is beyond the scope of the current work.

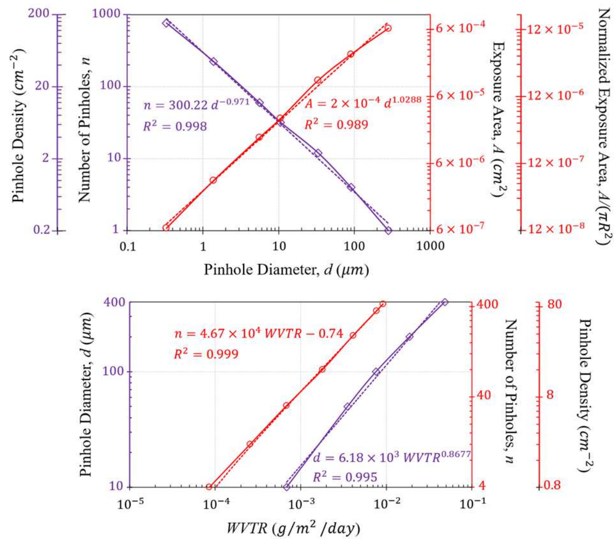

Fig. 3. The number of pinholes and their sizes distributed through the film predicting 8×10^{-4} g/m^2/day WVTR (Top) and the variation of the WVTR with the change of pinhole size and number of pinholes (Bottom). Note that *x*- and *y*- axes are in the logarithmic scale. Each data with a solid line displays a power trendline (Dashed lines).

VI. Conclusion

It is time consuming and costly process to continuously monitor defect distributions experimentally in terms of effort and money. The variations of WVTR depending on pinhole defect sizes and densities are investigated computationally and show logarithmically linear increase of WVTR. This work is still in progress to build data base of structure-property-performance relationship of small/extreme mismatch interface for flexible electronics encapsulation. We plan to continue upgrading the computational framework by incorporating it with external loadings, stochastic pinhole distributions, and other mechanical damages such as delamination and cracking.

Acknowledgment

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