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Modeling nonlinear moisture diffusion in inhomogeneous media

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ABSTRACT

While moisture diffusion in microelectronic device and packaging has been studied for decades, the problems involving complex nonlinear moisture diffusion in multi-material assembly have not been fully studied. This paper has developed a general nonlinear diffusion model by adopting water activity, a continuous state variable, as the field variable. The generalized solubility is introduced, which is temperature- and water activity-dependent. The effective diffusivity is defined and derived in terms of generalized solubility and water activity. By comparing the water activity-based model with the existing various normalized models, the present theory can unify and generalize the current approaches. More importantly, the present model can solve both linear and nonlinear moisture diffusion in inhomogeneous material system without normalization. The commercial finite element software has been applied to solve the nonlinear generalized moisture diffusion problem using the analogy of water activity and temperature. A source code of user-defined subroutines in ABAQUS has been provided in the Appendix of the paper. The mathematical formulation and the numerical implementation method presented in this paper can be applied to any nonlinear sorption or diffusion problems in inhomogeneous material system.

1. Introduction

Polymeric materials are widely used to make today's microelectronic devices in wafer processing, packaging, and encapsulations. One undesired characteristic is that polymeric materials inevitably absorb certain amount of moisture from the ambient. The absorbed moisture can lead to many deleterious effects, including material aging [1], hygroscopic swelling [2], electrochemical migration [3], and even popcorn failures [4–9]. Thus, studying moisture diffusion is crucial for the reliability of microelectronics, and has become a major focus of numerous research works [10–13].

To model moisture diffusion, Fick's law has been widely used, assuming that moisture flux is driven by the gradient of moisture concentration. The mathematical equation for Fickian moisture diffusion can be written as

$$\begin{aligned} &\mathbf{J} = -D_0 \nabla(C) \quad Fick's\ law; && (a)\\ &\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J} \quad Law\ of\ mass\ conversation && (b) \end{aligned} \tag{1}$$

where $\mathbf{J}$ is water flux, C is moisture concentration and D_0 is moisture diffusivity, which typically is a constant at a given temperature. For multi-material systems like electronic packaging, however, moisture concentration is discontinuous at the material interface due to distinct absorption capabilities of materials, as shown in Fig. 1a. As a result, Eq. (1) cannot be solved directly using field variable moisture concentration C [14–17]. To overcome the limitation, a common practice is to transform Eq. (1) by adopting a continuous field variable through normalization, as shown in Fig. 1b.

Different approaches have been developed in the literature, including the wetness theory [18], partial pressure technique [19], advanced normalization concentration approach [20], and direct concentration approaches such as Surface Humidity Potential (SHP) method [21]. According to a recent review [22], the wetness theory was considered more general than the other normalized theories. However, it may still encounter discontinuity issue when dissimilar materials have various temperature-dependent saturated moisture concentration. In addition, current normalization schemes are largely based on Henry's law, which is a linear relationship between saturated water concentration and relative humidity. Markus, et al. [21] proposed a Surface Humidity Potential (SHP) method to deal with non-Henry sorption behavior, but the nonlinear sorption relationship was only applied to the material surface or interface in the method.

This paper proposes a nonlinear diffusion model that can be used directly for heterogeneous system without the need of normalization. Water activity, which is a thermodynamic state variable and always continuous, is adopted as field variable. A water activity-based diffusion theory is formulated using the fundamental nonlinear diffusion equation with a generalized sorption isotherm theory. The generalized theory calculates moisture concentration as a product of water activity and generalized solubility. Determination of the generalized solubility and

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Nomenclature

J	water flux vector, kg/s/m^2
C	moisture concentration, kg/m^3
D_0	diffusivity, m^2/s
D_{eff}	effective diffusivity, m^2/s
B	mobility of water molecules, mol × m^2/s/J
γ	activity coefficient, m^3/kg
μ_w	water chemical potential, J/mol
a_w	water activity, dimensionless
p_{amb}	ambient partial pressure of water vapor, Pa
p_g	saturated water vapor pressure, Pa
K, K^H	generalized solubility, and generalized Henry's solubility, kg/m^3
C_{sat}	saturated moisture concentration, kg/m^3
S, S^H	solubility coefficient, and Henry solubility coefficient, kg/m^3/Pa
w	wetness, C/C_{sat}, dimensionless
p_s	normalized pressure term, Pa
ϕ	advanced normalized concentration, dimensionless
M	modified solubility, dimensionless
c_T	specific heat capacity, J/K/kg
k_T	thermal conductivity, W/m/K
r	volumetric heat source, W/m^3
E_D	activation energy for diffusivity, J/mol
E_S	activation energy for solubility, J/mol
E_b	activation energy for Langmuir hole affinity constant, J/mol
C_H'	Langmuir hole concentration constant, kg/m^3
b	Langmuir hole affinity constant, Pa^{-1}
i	subscript i refers to the material identification number

effective moisture diffusivity can be achieved by conducting sorption tests at various humidity and temperature conditions. The paper is organized as follows. The detailed model development is given in Section 2. Section 3 shows the use of the new model can unify the existing normalized models and furthermore serves as nonlinear diffusion model. Section 4 derives the effective diffusivity due to the nonlinearity of moisture diffusion. Section 5 validates the new model and provides a case study with non-Henry sorption isotherm material. The solutions are obtained in commercial finite element analysis package using the activity-temperature analogy.

2. Theory

Generally, mass diffusion could have many driving forces, such as the gradients of chemical potential, temperature and hydrostatic stress [13]. In this paper, we limit our scope to the mass diffusion driven by the gradient of chemical potential for clarity purpose. The consideration of the other driving forces will be reported in future work.

2.1. Fundamental equations

Consider a multi-material system subjected to dynamic humidity and temperature conditions, as shown in Fig. 2. The system contains multiple solid solvents with different chemical compositions and properties, representing a typical electronic assembly. Each solid (solvent) is able to absorb and transport moisture from the ambient. Without losing the generality, the isothermal condition is assumed throughout the system so that thermal diffusion is neglected.

As shown in Fig. 2, the thermodynamic state of water in a solid is characterized by the chemical potential μ_w. At a time and location, the chemical potential of water can be expressed in terms of two state variables, temperature T and water activity a_w, as [23–25]

$$\mu_w = \mu_{w0} + RT \ln a_w \tag{2}$$

with μ_{w0} is the standard chemical potential and R is universal gas constant. Water activity a_w is a thermodynamic term for describing the availability of water, a well-adopted concept on food and membrane systems [25–31]. The water activity of a moisture-solid (water-solvent) system *at equilibrium* can be determined by the following equation [25,27,32].

$$a_{w,eq} = p_{amb}/p_g \equiv RH \tag{3}$$

where p_{amb} is the partial water vapor pressure of the ambient that contacts with the system, and p_g is saturated water vapor pressure. Therefore, the water activity of an equilibrium system can be directly determined by measuring the RH, except that RH is usually expressed in percentage.

To describe moisture diffusion in multi-material system, the fundamental equation for water flux, **J**, should be used [23,24]

$$\mathbf{J} = -C_i \mathbf{v}_i = -C_i (B_i \nabla \mu_w). \tag{4}$$

Here, the subscript "i", refers to the identification number of material, is used in those discontinuous variables such as C_i (kg/m^3), the moisture concentration, $\mathbf{v}_i$, the solute transport velocity, and B_i, the mobility of water molecules in solvent i. Since **J** and μ_w are always continuous, subscript "i" is not used. This rule will be applied throughout the following derivations. Eq. (4) states that zero water flux exists only when the chemical potential of water is the same everywhere.

While the chemical potential is continuous, it is difficult to unitize Eq. (4) for engineering applications. Since water activity is also a continuous state variable, one can replace the chemical potential by water activity in Eq. (4) without losing the continuity requirement. Substituting

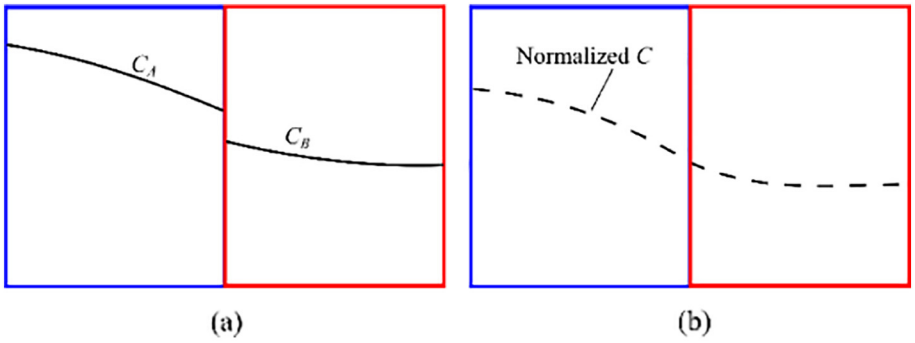

Fig. 1. Illustration of a bi-material system with (a) discontinuous moisture concentration and (b) continuous normalized concentration.

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