Phase-field modeling of the effect of interfacial energy on pyrolytic carbon morphology in chemical vapor deposition

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A conserved phase-field model is proposed to investigate the effect of interfacial energy on the morphological evolution of the pyrolytic carbon deposit in chemical vapor deposition. The equilibrium geometry of carbon deposit islands is analytically predicted, of which the contact angle was controlled through the boundary conditions of the phase-field parameter at the substrate surface according to the Young-Laplace equation. Simulations of deposit growth are carried out for single and multi island nucleation. It is clarified that the island morphology depends on the magnitude of the interface energy. It is also observed that high interface energy results in large island size fluctuation.

1 Introduction

In meso scale, few studies focus on the influence of surface roughness and surface energies of substrates on the growth morphology of three-dimensional carbon deposit islands shown in Fig.1(a). In the present work, a conserved phase-field model is proposed to describe the growth of carbon deposit islands in contact with gas-phase precursors taking into account the interfacial energies.

2 Phase-field model

Fig.1(b) shows a typical configuration of a partially wetting carbon deposit on a substrate surrounded by the gas-phase precursor. Generally, three conserved ordered parameters, \( \phi_1 \), \( \phi_2 \), and \( \phi_3 \) representing the volume fractions of gas-phase precursor, carbon deposit, and substrate, respectively, have to be introduced to model island growth. Assuming the surface morphology of the substrate does not change with progressing deposition, a certain boundary condition \( \phi_a \) can be applied on the interface between the gas-phase and the substrate to replace the independent ordered parameters, \( \phi_3 \) as shown in Fig.1(c). Since the relation \( \phi_1 + \phi_2 + \phi_3 = 1 \) must be satisfied at all local points, therefore one independent variable \( \phi \) is enough to describe the carbon deposit. The total free energy of the system is given in details in [1]. An equilibrium interface solution between gas precursors and carbon deposit is found at \( \delta, G = 0 \). The interfacial energies of the three-phase system can then be calculated by the integration of the gradient energy in the interfaces:

\[
\gamma_{gd} = \int_{-\infty}^{\infty} (\varepsilon^2 \nabla^2 \phi) d\nu = \int_0^1 4\sqrt{2\varepsilon^2 w\phi(1-\phi)} d\phi = \frac{2\sqrt{2\varepsilon^2 w}}{3},
\]

\[
\gamma_{sg} = \int_0^{\phi_s} 4\sqrt{2\varepsilon^2 w\phi(1-\phi)} d\phi = \frac{2\sqrt{2\varepsilon^2 w}}{3} [3\phi_s^2 - 2\phi_s^3],
\]

\[
\gamma_{ds} = \int_{\phi_s}^1 4\sqrt{2\varepsilon^2 w\phi(1-\phi)} d\phi = \frac{2\sqrt{2\varepsilon^2 w}}{3} [1 - 3\phi_s^2 + 2\phi_s^3],
\]

where \( \gamma_{gd} \) denotes the gas-deposit interfacial energy, \( \gamma_{sg} \) the substrate-gas interfacial energy, and \( \gamma_{ds} \) the deposit-substrate interfacial energy, \( w \) the energy barrier between the gas-phase precursor and the carbon deposit, \( \varepsilon^2 \) the gradient-energy coefficient. Based on the Young-Laplace equation, the contact angle \( \theta \) shown in Fig.1(c) can be expressed as \( \cos(\theta) = \frac{6\phi_s^2 - 2\phi_s^3}{1 - 3\phi_s^2 + 2\phi_s^3} \). Calculations show that higher textural similarity of the meso-phase droplet with the substrate improves the wettability of carbon deposit island on the substrate. The time evolution of \( \phi \) with carbon deposition is predicted using the Cahn-Hilliard equation [2]:

\[
\phi_t = \nabla \cdot (M \nabla \nu) + u_n |\nabla \phi|, \quad \nu = f_\phi - \varepsilon^2 \nabla^2 \phi,
\]

where a deposition interface growing exclusively with a constant normal interface speed, i.e. \( u = u_n n \) is considered. \( M \) is the phase field mobility representing the surface diffusion, \( f \) is the local free energy density and a simple double well function,
Fig. 1 Growth of three-dimensional deposit islands in CVD of pyrocarbon (a). A partially wetting carbon deposit presented with three field-phase parameters (b), with one field-phase parameter (c).

Fig. 2 Influence of the interfacial energies on the morphology of a single deposit island growing via heterogeneous nucleation (a-b), the growth of multi deposit islands (c-d).

i.e. \( f_\phi = 16\phi^2(1-\phi)^2 \). The fourth-order partial differential equation shown in Eq.(4) is solved with finite element methods based on its weak form shown in Eq.(5).

\[
\int_\Omega (\varepsilon^2 \nabla \phi \cdot \nabla \phi) d\Omega - \int_{\partial \Omega} \mathbf{n} \cdot (\varepsilon^2 \nabla \phi) \text{test}(\phi) ds + \int_\Omega (f_\phi - \nu) \text{test}(\phi) d\Omega = 0; \\
\int_\Omega \phi_\text{test}(\nu) d\nu + \int_\Omega (M \nabla \phi) \cdot n \cdot (M \nabla \phi) \text{test}(\nu) d\nu - \int_{\partial \Omega} \mathbf{n} \cdot (M \nabla \phi) \text{test}(\nu) ds - \int_\Omega (u_n |\nabla \phi|) \text{test}(\nu) d\nu = 0.
\]

Fig.2(a) and (b) illustrate the influence of the interfacial energies on the morphology of a single deposit island growing via heterogeneous nucleation. It is clear that a higher gas-substrate interfacial energy leads to a better wettability of carbon deposit on the substrate shown in Fig.2(a), while higher microstructural similarity of the meso-phase carbon deposit with the substrate results in a higher growth rate of carbon deposit shown in Fig.2(b). Fig.2(c) and (d) illustrate the influence of the interfacial energy on the growth of multi deposit islands. It is observed that a large island size fluctuation is inducted by high interface energies.

3 Conclusions

The morphological evolution of the pyrolytic carbon deposit is modeled with a conserved phase-field model. The model is able to describe the formation dynamics and equilibrium geometry of carbon deposit islands. It is clarified that higher textural similarity of the meso-phase droplet with the substrate helps to improve both the wettability and the growth rate of carbon deposit island on the substrate.

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References