Stress-driven surface instabilities in solids with diffusing charged defects

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1. Abstract

Stress-driven rearrangement instability (SDRI) theory postulates that diffusion in stressed solids can lead to surface morphological instability, an effect that is currently believed by many physicists to be real and important for elevated-temperature deposition or annealing of thin films. Both atomic surface diffusion and bulk diffusion of point defects contribute to the instabilities. The stress-driven diffusion of mobile oxygen vacancies in the bulk is especially important in ferroic perovskite films (e.g., Barium Strontium Titanate), which have desirable optical and electric properties for device and sensor applications, and often require well-controlled surfaces and interfaces. We present a continuum reformulation of the SDRI theory that includes the coupled electro-elastic diffusion of oxygen vacancies and introduce a 3D finite-element scheme to solve the equations for film surface evolution. We also explore the stability of the film boundary due to perturbations and attempt to characterize the incipient instabilities in terms of the model parameters.

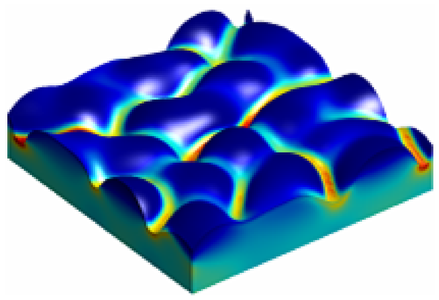


Figure 1: *Simulated image of thin film surface roughness.*

2. Balance Equations

Here, we state the balance laws required in deriving our constitutive model. Electrostatic interactions are governed by Maxwell's equations

$$D_i = \epsilon_0 E_i + P_i \tag{1}$$
$$D_{i,i} = \hat{\rho} \tag{2}$$
$$E_i = -\phi_{,i} \tag{3}$$

where D_i is the electric displacement, ϵ_0 is the permittivity of free space, E_i is the electric field, P_i is the polarization, ϕ is the electrostatic potential, and $\hat{\rho}$ is the enclosed charge density. Mass conservation in the bulk and at the free surface yield the following relationships

$$Q_{i,i} = -\dot{\xi} \tag{4}$$
$$\dot{a}(1-\alpha\xi) = -\alpha(Q_i n_i + q_{\alpha,\alpha}) \tag{5}$$

where the dot operator represents the material time derivative, ξ is the vacancy number concentration, Q_i is the bulk vacancy flux, $\dot{a}$ is the normal velocity of the free surface, α is the atomic volume, and $q_{\alpha,\alpha}$ is the surface diffusive flux. We also assume mechanical equilibrium

$$\sigma_{ij,j} = 0 \tag{6}$$

where we neglect the influence of any body forces.

3. Constitutive Theory

Here, we develop a thermodynamically-consistent model for a material with mobile charged vacancies using the Coleman-Noll procedure. We assume that the charge density is proportional to the vacancy concentration through the elementary charge e and vacancy valance contribution z.

$$\hat{\rho} = ez\xi \tag{7}$$

Based upon the second law of thermodynamics, the dissipation rate is always non-negative for any thermodynamically-admissible process.

$$\Phi = W - \dot{\Omega} \geq 0 \tag{8}$$

We assume the following expressions for the external working rate W and total system energy rate Ω

$$\begin{aligned} W &= \frac{D}{Dt}\int_s (\text{electric} + \text{interfacial} + \text{mechanical} - \text{chemical})\, ds \\ &= \frac{D}{Dt}\int_s \left(\bar{\sigma}\phi + \tau\kappa + \hat{t}_i u_i - \mu Q_i n_i\right) ds \end{aligned} \tag{9}$$

$$\begin{aligned} \Omega &= \int_v (\text{internal} + \text{electric})\, dv \\ &= \int_v \left(\rho U + \frac{\epsilon_0}{2}\|\phi_{,i}\|^2\right) dv \end{aligned} \tag{10}$$

we write U in terms of the Helmholtz free energy of the system Ψ, which is assumed to have a functional dependence on strain, polarization, temperature, and vacancy concentration, and defined in the usual way.

$$\Psi = \Psi(u_{(i,j)}, P_i, \theta, \xi) = U - \theta\eta \tag{11}$$

Employing this definition of Ψ and the previously stated balance laws, we mathematically enforce non-negativity on each process in the resulting equation to extract our constitutive relationships.

$$\eta = -\frac{\partial\Psi}{\partial\theta} \tag{12}$$
$$E_i = \rho\frac{\partial\Psi}{\partial P_i} \tag{13}$$
$$\sigma_{ij} = \rho\frac{\partial\Psi}{\partial u_{(i,j)}} \tag{14}$$
$$\hat{t}_i = \rho\frac{\partial\Psi}{\partial u_{(i,j)}}n_j \tag{15}$$
$$Q_i = -d_{ij}\mu_j^B \tag{16}$$
$$\mu^B = \rho\frac{\partial\Psi}{\partial\xi} + ez\phi \tag{17}$$
$$Q_i n_i = \beta(\mu^S - \alpha^{-1}\mu^B) \tag{18}$$
$$q_\alpha = -A_{\alpha\beta}\mu_\beta^S \tag{19}$$
$$\mu^S = \frac{\rho\Psi + \rho\phi - \tau\kappa}{1-\alpha\xi} \tag{20}$$

To proceed, we must assume an explicit form for the Helmholtz free energy.

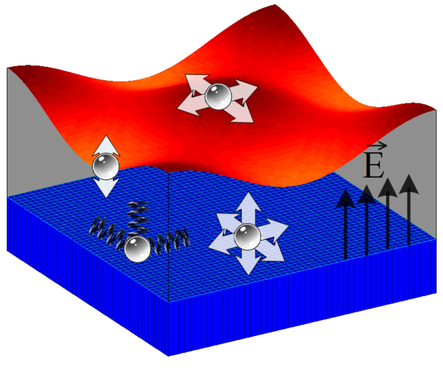


Figure 2: *Cartoon depiction of film processes under consideration.*

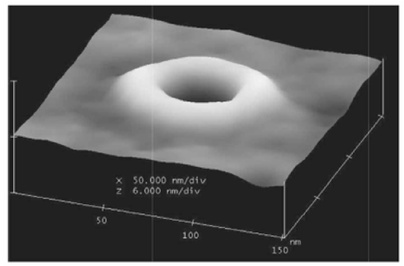


Figure 3: *AFM image of a single CuO ring on $SrTiO_3$ substrate.*

4. Free Energy #1 (El-Azab and Liang, 2003)

If we neglect electrostatics and bulk diffusion, this theory corresponds with El-Azab and Liang (2003).

$$\rho\Psi = \frac{1}{2}C_{ijkl}u_{(i,k)}u_{(j,l)} \tag{21}$$

In that work, the authors demonstrate the formation of nanoscale rings from surface pits, dot-dot coalescence, and a ring-to-dot transition.

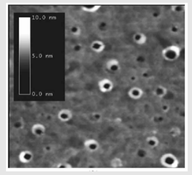
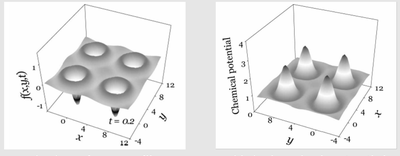


Figure 4: *AFM image of Cu/$SrTiO_3$ film morphology after plasma exposure*



(a) surface profile (b) chemical potential

Figure 5: *Simulation of a square array of rings*

5. Free Energy #2

We propose the following extended free energy term that we hope will capture additional physics, most importantly the influence of charged vacancies:

$$\rho\Psi = \frac{1}{2}C_{ijkl}u_{(i,k)}u_{(j,l)} + \frac{1}{2}\lambda_{ij}P_iP_j - \frac{1}{3}\sigma_{ii}\delta + \varphi(\xi,\theta) \tag{22}$$

with elastic coefficients C_{ijkl}, electric susceptibility λ_{ij}, relaxation volume δ, and the free energy of vacancies $\varphi(\xi,\theta)$ for which we assume

$$\begin{aligned} \varphi(\xi,\theta) &= E^v\xi + k_B\ln(\xi!(1-\xi)!) \\ &\approx E^v\xi + \alpha^{-1}k_B\theta\left((1-\alpha\xi)\ln(1-\alpha\xi) + \alpha\xi\ln\alpha\xi\right) \end{aligned} \tag{23}$$

where E^v is the vacancy formation energy and we have made use of Sterling's approximation

$$\ln N! \approx N\ln N - N \tag{24}$$

6. Method of Solution

Here, we state the resulting governing equations in weak form, appropriate for use in a finite element program.

6.1 Electrostatics

Given: $\hat{\rho} : \Omega \to \mathbb{R}$, $V : \Gamma_V \to \mathbb{R}$ and $D_i n_i : \Gamma_D \to \mathbb{R}$, find $\phi \in \mathscr{S}$ such that $\forall\, w \in \mathscr{V}$

$$-\int_{\Gamma_D} wD_i n_i\, d\Gamma - \int_\Omega w_{,i}\epsilon_{ij}\phi_{,j}\, d\Omega + \int_\Omega w\hat{\rho}\, d\Omega = 0 \tag{25}$$

where,

$$\phi = V \text{ on } \Gamma_V \tag{26}$$

6.2 Elasticity

Given $f_i : \Omega \to \mathbb{R}$, $\bar{u}_i : \Gamma_u \to \mathbb{R}$ and $\hat{t}_i : \Gamma_{\hat{t}} \to \mathbb{R}$, find $u_i \in \mathscr{S}$ such that $\forall w \in \mathscr{V}$

$$\sum_{i=1}^{n_{sd}}\left(\int_{\Gamma_{\hat{t}_i}} w_i\hat{t}_i\, d\Gamma\right) - \int_\Omega w_{i,j}\sigma_{ij}\, d\Omega + \int_\Omega w_i f_i\, d\Omega = 0 \tag{27}$$

where,

$$u_i = \bar{u}_i \text{ on } \Gamma_u \tag{28}$$

6.3 Diffusion

Given $\Delta t > 0$, $\gamma \in (0,1)$, $\xi^n : \Omega \to \mathbb{R}$, $\bar{Q}_i : \Gamma_Q \to \mathbb{R}$, and $Q_i n_i : \Gamma_{Qn} \to \mathbb{R}$, find $\xi^{n+1} \in \mathscr{S}$ such that $\forall\, w \in \mathscr{V}$

$$\begin{aligned} 0 &= \int_\Omega w\xi^{n+1}\, d\Omega - \int_\Omega w\xi^n\, d\Omega \\ &+ (1-\gamma)\Delta t\left(\int_{\Gamma_{Qn}} wQ_i^n n_i^n\, d\Gamma - \int_\Omega w_{,i}Q_i^n\, d\Omega\right) \\ &+ \gamma\Delta t\left(\int_{\Gamma_{Qn}} wQ_i^{n+1}n_i^{n+1}\, d\Gamma - \int_\Omega w_{,i}Q_i^{n+1}\, d\Omega\right) \end{aligned} \tag{29}$$

where,

$$Q_i = \bar{Q}_i \text{ on } \Gamma_Q \tag{30}$$

6.4 Free Boundary Update

We update the free surface profile using the relation

$$r_n = r_n + \dot{a}\Delta t \tag{31}$$

where $\dot{a}$ is given by (5).

7. Ongoing Work

- Continuum model for oxygen vacancies in ferroic perovskites
- Fully three-dimensional finite element implementation
- Verification and validation of computer code
- Analysis of numerical results

8. References

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