

Evaluation of the Surface Tension of Silicon-Gold Binary Liquid Alloy

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Abstract. The gold-catalyzed vapor-liquid-solid (VLS) method is widely used for silicon nanowire (Si NW) fabrication. As the VLS process is influenced by the physical properties of the catalytic silicon-gold (Si-Au) droplet, quantifying the surface tension of the liquid alloy is important to achieve better control of the wire growth. Because the experimental measurement of the surface tension is difficult, it is necessary to obtain reasonable estimates from computational models. In this work, we conducted molecular dynamics simulations with a modified embedded-atom potential developed for the Si-Au binary system, and evaluated the surface tension γ based on the Virial stress expression. The dependence of surface tension γ on the Si fraction χ and temperature T is predicted. The entropy of the liquid-vapor interface was extracted from the slope of the γ - T curve. The Si concentration and stress distributions near the surface are also predicted. Our surface tension evaluation enables theoretical predictions of droplet and nanowire shape, and provides physical inputs for continuum phase-field models of VLS growth.

Introduction

Silicon nanowires (Si NWs), as the components of the next generation electronic devices, have promising applications in many fields, due to their special electrical and optical properties [1]. The gold-catalyzed vapor-liquid-solid (VLS) method is commonly used for Si NW fabrication. This process requires a gold-silicon binary liquid droplet that can absorb the Si atoms from the vapor phase, transport the materials to the solid-liquid interface through diffusion, and finally reach a supersaturated state resulting in the nucleation at the interface. The surface tension, as one of the important physical properties of the liquid droplet, plays a key role in controlling the size, shape and quality of the NW grown in the VLS manner. The surface tension depends on many factors such as the Si fraction and temperature; hence it is important to obtain their values under different conditions. However, the measurement of the surface tension in experiments is usually difficult and the results in literature have a significant variation with different experimental techniques and environment [2]. Therefore, estimation from the atomistic simulation would be a necessary complement to the experiments. Typically there are two approaches to evaluate surface tension from molecular dynamics simulations [3]. One is the thermodynamic method that calculates the surface tension from the Helmholtz (or Gibbs) free energy of the system. It requires appropriate reaction coordinates and special sampling methods. The other is the mechanical method that extracts the surface tension from the Virial stress. Compared to the free energy method, the mechanical method is usually more efficient and easier to implement.

In this work, we adopted the second approach to evaluate the surface tensions for the Si supersaturated liquid Si-Au system alloy. The simulation predictions are comparable to existing data in the literature. The paper is organized as follows. The Virial stress formulation and the molecular dynamics (MD) simulation setup are explained in the *Method* Section. The simulation results, including the stress distribution, the surface tension prediction as a function of temperature and Si fraction, and the surface entropy estimation are discussed in the *Results and discussions* Section. In the *Summary* Section, we summarize the results and discuss their potential applications.

Method

Surface Tension from Virial Stress. The Virial stress formula predicts the macroscopic stress tensor corresponding to a molecular dynamics (MD) simulation cell. The expression for the $\sigma_{\alpha\beta}$ component of the stress tensor is given by Eq. 1 [4]. Where α and β correspond to X, Y or Z for a Cartesian coordinate system in 3D.

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \sum_{i \text{ in } \Omega} \langle -m^{(i)}(u_{\alpha}^{(i)} - \bar{u}_{\alpha})(u_{\beta}^{(i)} - \bar{u}_{\beta}) + \frac{1}{2} \sum_j (x_{\alpha}^{(j)} - x_{\alpha}^{(i)}) f_{\beta}^{(ij)} \rangle. \quad (1)$$

In Eq. 1, Ω is the volume of the simulation cell. $m^{(i)}$ is the mass of the i -th atom. The average velocity is denoted as \bar{u} with the subscript α or β specifying its direction, while $u^{(i)}$ represents the velocity for each individual atom i . Similar notations are applied to the second term in the angular bracket. For example, $x_{\alpha}^{(j)}$ is the α component of the position vector of the atom j and $f_{\beta}^{(ij)}$ is the β component of the force on atom i by atom j . The angular brackets correspond to ensemble average, which is usually approximated by the time average in MD simulations.

Assuming a system of liquid with surfaces exposed to vacuum, for example, a liquid thin film spreading in the X-Z plane with the surface normal pointing to the Y direction, all the non-diagonal elements of the surface tensor matrix should be zero. The σ_{yy} component should also be zero in the absence of external forces. Thus, the surface tension γ can be evaluated from the stress tensor by Eq. 2,

$$\gamma = \frac{1}{2} L_y \bar{\sigma}_{inplane}, \quad (2)$$

where L_y is the height of the simulation box along Y direction, $\bar{\sigma}_{inplane} = \frac{\bar{\sigma}_{xx} + \bar{\sigma}_{zz}}{2}$ is the average in-plane stress on the surface, and the factor of $\frac{1}{2}$ accounts for the two surfaces of a free-standing liquid film.

Simulation Setup. The molecular dynamics simulation package MD++ [5] was used to perform the simulation. We adopted a modified-EAM potential [6] designed for the Si-Au system that has the ability to construct the binary phase diagram comparable to experimental data (shown in Fig. 1(a)). The molecular dynamics simulations were conducted at temperatures of 700K, 800K, 900K and 1000K, and with Si fraction of 25%, 30%, 35%, 40%, 45%, 50% and 55% for each temperature condition. The simulation conditions are shown as filled circles on the Si-Au binary phase diagram in Fig. 1(a). For each simulation, a simulation cell containing 6912 atoms was initialized with the specified Si fraction. Periodic boundary conditions were applied along all three (X, Y and Z) directions. Simulations using the isothermal-isobaric ensemble were then performed for 10^6 steps to equilibrate the system to zero stress. Nosé-Hoover thermostat and Parinello-Rahman barostat were used for temperature and pressure control, respectively. At the end of this simulation, we enlarged the length of the simulation box along Y direction, while maintaining the real coordinates of the atoms. This led to free surfaces normal to the Y direction while periodic boundary conditions were still kept for the X and Z directions. After this adjustment, MD simulations were run for another 4×10^6 steps under the canonical ensemble and the Virial stress was calculated every 100 steps. The time average of the Virial stress is computed after the stress has reached equilibrium.

Results and Discussions

Si Fraction and Stress Distribution. It is necessary to confirm the system is already converged before we start the surface tension calculation. A qualitative analysis can be done by visually observing the atoms arrangement. For example, Fig. 1(b) shows a side view of the atoms configuration with the Si fraction of 40% at 700K after 100,000 steps run. From the figure we can clearly identify the black colored Si atoms and the yellow colored Au atoms that are well mixed. To

quantify the atomic distribution, we collect 50 atoms configurations at different simulation steps, and plot the average Si fraction distribution along Y direction in Fig. 2(a). It shows the Si fraction at different position fluctuates around the designate 40% with a small magnitude, which further verifies the atoms reach a uniform distribution.

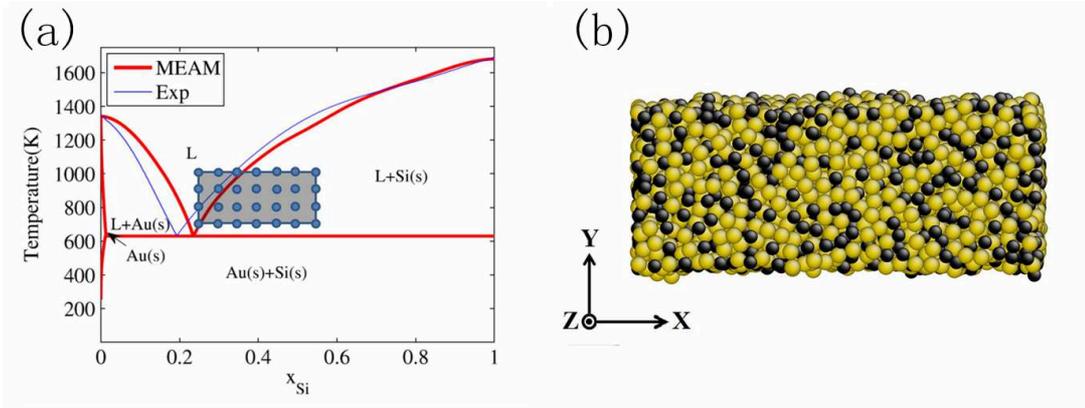


Fig. 1 (a) Phase diagram of the Si-Au system where the filled circles showing the simulation conditions. (b) Side view of the atoms configuration with the Si fraction of 40% at 700K, visualized using Atomeye [7].

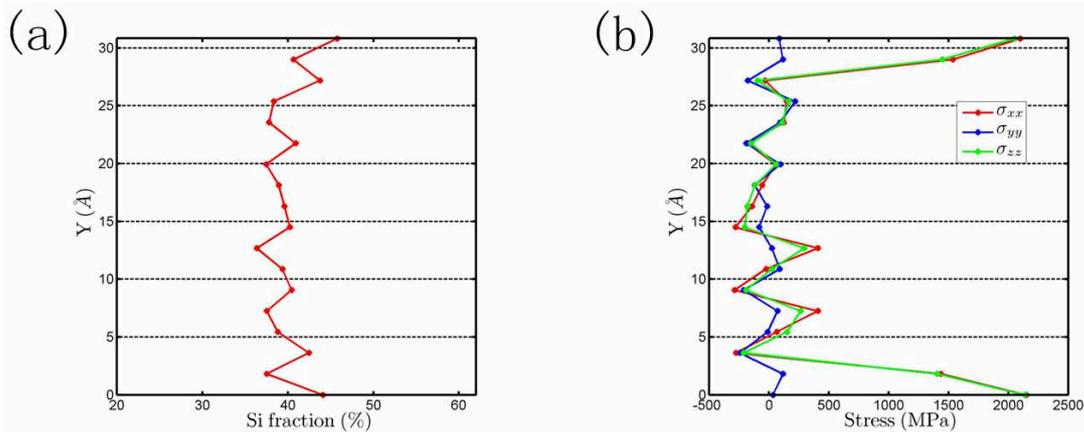


Fig. 2 (a) The Si fraction distribution along Y direction, and (b) the stress distribution along Y direction.

We also examine the distribution of all the normal stress components as a function of Y, as shown in Fig. 2(b). We can find from the figure that σ_{yy} fluctuates around 0 as expected, since the free surface is along the Y direction. The distributions of σ_{xx} and σ_{zz} have a very similar behavior due to the isotropy of the liquid surface in the X and Z directions. The non-zero stress contribution is only appreciable at the two regions near the top and bottom surfaces. The stress inside the material is around zero, indicating that the system has been well equilibrated.

Surface Tension Calculation. The evaluation of the surface tension is based on Eq. 2. Among the input parameters of the expression, the height of the simulation box is known, and the stresses are computed by the following procedure. For each temperature and Si fraction condition, after the first one million steps NVT simulation, the Virial stress components σ_{xx} and σ_{zz} are calculated using Eq. 1 at every 100 steps. The time averages of those instantaneous Virial stresses are taken every 10^6 steps, till the simulation ends at 4×10^6 steps. The means of the time averages are used to determine $\bar{\sigma}_{xx}$ and $\bar{\sigma}_{zz}$ and the standard deviations are computed to estimate the error. The predicted values of the surface tension all fall within a region of [0.5, 0.75] N/m, consistent with the measured values for the Si-Au alloy at the eutectic compositions in the literature [8].

Surface Tension as Functions of Temperature and Si Fraction. Fig. 3 plots the surface tension values as a function of temperature at different Si fractions. The figure shows that the surface tension tends to decrease with raising temperature for all the Si fraction conditions in our simulations. As the surface tension is equivalent to the surface free energy per unit area for the liquid, the decrease of surface tension corresponds to positive entropy.

The Helmholtz free energy has the expression of

$$F = E - TS, \quad (3)$$

where E is the internal energy and S is the entropy. The main contribution to the internal energy is from the bonding that is not sensitive to temperature change. Assuming entropy is insensitive to temperature, we would expect the free energy to decrease linearly with temperature, which is consistent with the data shown in Fig. 3. This comparison reveals a link between the surface entropy and the γ - T curve, which will be discussed later in this section in details.

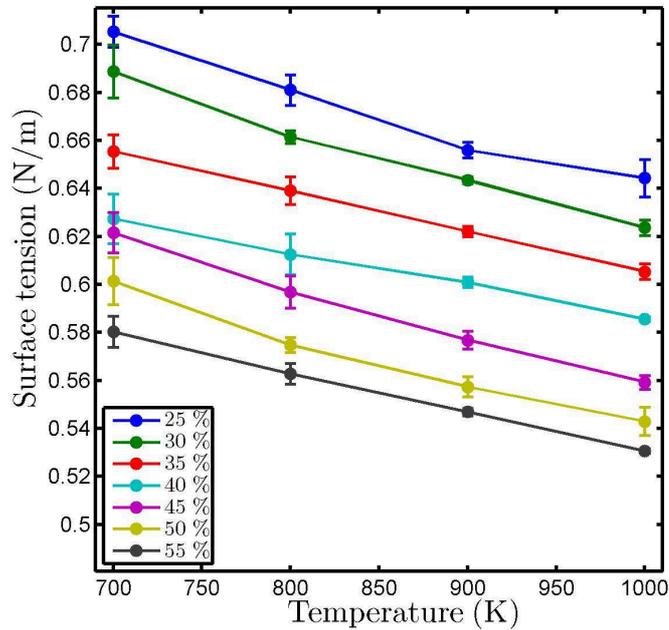


Fig. 3 Surface tension as a function of temperature at different Si fractions

The surface tension's dependence on the Si fraction is shown in Fig. 4. From the figure we can find the surface tension tends to decrease (almost linearly) with increasing Si fraction. Because the surface tension of liquid gold [9] is higher than that of liquid silicon [2], this trend is consistent with a simple model in which the surface tension of the Si-Au alloy is considered as a linear combination of the surface tension of pure liquids.

We propose a function form that expresses the surface tension's dependences on Si fraction and temperature by a single equation,

$$\gamma(\chi_{Si}, T) = a + b\chi_{Si} + cT, \quad (4)$$

where $a = 0.9282 \text{ J/m}^2$, $b = -0.004014 \text{ J/m}^2$ and $c = -0.0001844 \text{ J/(m}^2 \cdot \text{K)}$ are the three fitting parameters. The R-square value of this fitting procedure is 0.99, which means the chosen linear equation fits the data points very well. The lack of higher order terms in Eq. 4 means that the surface entropy is relatively insensitive to Si fraction. From the two-dimensional fitting function of Eq. 4, the surface entropy of the Si-Au liquid is estimated to be $0.1844 \text{ mN/(m} \cdot \text{K)}$.

Given the number of surface atoms in our simulation cell (around 550 atoms) and the surface area (49 nm^2), the surface entropy of the Si-Au liquid is about $1.19 k_B$ per surface atom. Although there is lack of experimental data for the surface entropy of the Au-Si binary system for us to compare with, our estimate is comparable to the value reported for pure liquid silicon, which is $0.99 k_B$ per surface atom [8].

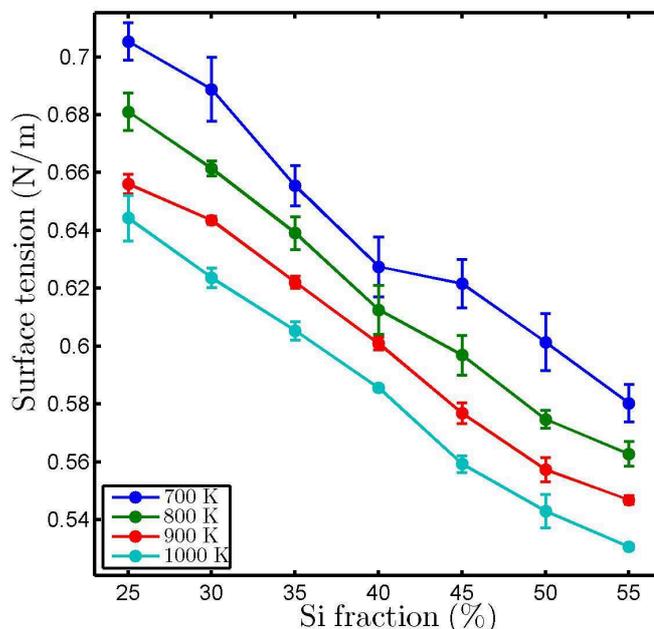


Fig. 4 Surface tension as a function of Si fraction at different temperatures

Summary

In this work, we perform atomistic molecular dynamics simulations for a Si-Au binary liquid alloy system in the Si-supersaturated conditions and evaluate the surface tension γ from the Virial stress. The predicted surface tensions are in good agreement with the existing experimental data. We show the surface tension γ decreases linearly with both increasing temperature and increasing Si fraction. The extracted surface entropy value is comparable to existing estimates for pure liquid silicon. These results provide a fundamental input needed by continuum models (such as the phase field method) to predict droplet and nanowire shape during VLS growth. In the future, we would like to predict the liquid-solid interfacial energy for the Au-Si binary system from atomistic simulations, which is another important material parameter controlling VLS growth.

Acknowledgements

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