

Statistical properties of interface stress of amorphous silicon

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Summary

Surface energy and surface stress is a key parameter for predicting of the intrinsic stress of thin film. We have evaluated the statistical properties of the surface energy and the surface stress of amorphous silicon by using molecular dynamics (MD), and obtained values of 1.44 ± 0.03 J/m² and -0.48 ± 0.06 N/m for surface energy and surface stress, respectively. We placed particular emphasis on the statistical aspects of these two parameters. Since it has been determined that dispersion shows a normal distribution, that of an area of any size can be predicted by the central limit theory. It is known that the dispersion of surface stress is significantly large.

Introduction

The intrinsic stress (residual stress) of thin films induces delamination and generates dislocation at the interface. Therefore, the control of intrinsic stress is of great concern. Various studies have been performed to clarify the origins of intrinsic stress, and it has been found the intrinsic stress depends strongly on the microstructure and growth mode at the atomic level[1].

Real-time measurements of stress evolution during the deposition of thin films that grow under the Volmer-Weber (VW) mechanism have been carried out by Thompson et al[2]. In their works, Thompson et al. examine the evolution of stress and have determined that compressive stress is generated at an early stage and tensile stress is generated at a later stage. In the early stages of VW growth, since small crystal islands are strained by the surface and interface stress, the interatomic distance of each island varies with the size and shape of the island. With the increase in the island size, the constraint between substrate and island increases. This constraint leads to compressive stress in the islands[3]. Further increase in size results in the coalescence of islands. The key parameters of this coalescence are surface energy and interface energy. Several studies have shown that island coalescence induces tensile stress in the film by forming a new boundary under the substrate constraint[4]. Therefore, accurate evaluation of the surface energy and the surface stress is extremely important in order to predict the intrinsic stress of the thin films. Since it is considered rather difficult to obtain the values of surface energy and surface stress experimentally, numerical evaluation by molecular simulation has been attempted. Streitz and Gumbsch et al. calculated the surface and interface stress for several fcc metals using the molecular dynamics method[5][6].

On the other hand, it is well known that the intrinsic stress and the microstructure of thin film silicon depends greatly on the growth temperature and growth rate of the chemical vapor deposition (CVD) process, which is widely used in manufacturing semiconductor devices. Recently, transmission electron microscopic (TEM) observation has clarified the VW growth mechanism of polycrystalline silicon. At first the amorphous islands with a radius of 1-10 nm nucleate on the substrate, then they grow and coalesce while they are crystallized.

In this study, we used molecular dynamics to numerically calculate the value of the surface energy and the surface stress of amorphous silicon, which are critical parameters for intrinsic stress. We placed particular emphasis on the statistical aspects of these two parameters since the space-related dispersion of the parameter cannot be neglected. Finally, we conducted fundamental research on how to apply the parameters calculated at the atomic level to analyses for continuum mechanics.

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Surface energy and surface stress

Surface energy and surface stress are usually defined from the viewpoint of thermodynamics. For the investigation of intrinsic stress, however, these phenomena are closely related to finite strain. Therefore, a definition of these parameters that takes finite strain into account is introduced first.

Surface energy γ is defined by the increase of the energy per unit area when the surface is newly created [7], as represented in Eq. (1),

$$\gamma(\epsilon) = \frac{1}{A(\epsilon)} \left(E^{surf}(\epsilon) - E^{bulk}(\epsilon) \right) \quad (1)$$

where E^{surf} is the energy per unit cell for the surface model, E^{bulk} is the energy for bulk solid which contains the same number of atoms as the surface model, A is the surface area, and ϵ is the strain.

Surface stress is defined as the energy variation per unit area for a finite strain ϵ_{ij} :

$$\begin{aligned} f_{ij} &= \frac{1}{A_0} \left. \frac{\partial(A(\epsilon)\gamma(\epsilon))}{\partial\epsilon_{ij}} \right|_{\epsilon=0} \quad (i, j = 1, 2) \\ &= \frac{1}{A_0} \left(\left. \frac{\partial E^{surf}(\epsilon)}{\partial\epsilon_{ij}} \right|_{\epsilon=0} - \left. \frac{\partial E^{bulk}(\epsilon)}{\partial\epsilon_{ij}} \right|_{\epsilon=0} \right) \end{aligned} \quad (2)$$

for the standardization, the strain corresponding to the lattice parameter at a bulk stress of zero is defined as zero.

Method of calculation

In order to investigate the dispersion of the amorphous structure, the simulation cell size should be sufficiently large. For the purpose of this study, we chose a 27000-atom cell, whose size is about $8 \text{ nm} \times 8 \text{ nm} \times 8 \text{ nm}$, and the Tersoff potential [8] was used for the interatomic potential of the silicon. The structure of the amorphous silicon was produced by the melt-quench method. The validity of the two-body correlation function and the bond angle distribution function are confirmed by comparison with experimental results [9]. The surfaces are formed by cutting the bulk model parallel to the xy plane as shown in Fig. 1. To prevent rigid-body motion, the atoms which belong in the region within 0.5 nm from the bottom are fixed. After creating the surfaces, the systems are relaxed using the conjugate gradient (CG) method.

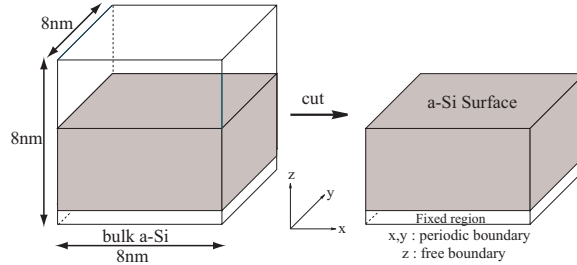


Figure 1: Molecular dynamics simulation model

To investigate statistical properties, 30 surfaces were produced randomly, and the mean value and the standard deviation of the surface energy and the surface stress were evaluated. The surface energy and the surface stress were calculated for both the non-relaxed surface without applying the CG method and the relaxed surface applying the CG method.

Results

The results obtained for the surface energy γ and the surface stress $f = (f_{xx} + f_{yy})/2$ of amorphous silicon are shown in Table 1. The results are shown according to the mean value and the standard deviation for 30 samples. The value of the Si(100) surface is also shown [10] for references. The upper row indicates the results obtained for the non-relaxed surface and the lower row indicates those of the relaxed surface. The results of surface stress f for c-Si(100) 2×1 are the values along the dimer bond f_{xx} and the rows of dimers f_{yy} .

Table 1: Surface energy and surface stress of amorphous silicon (upper: non-relaxed surface, lower: relaxed surface)

	α -Si	c-Si(100) 1×1	c-Si(100) 2×1
γ (J/m^2)	1.75 ± 0.04 1.44 ± 0.03	2.31 2.27	2.31 1.48
f (N/m)	0.29 ± 0.03 -0.48 ± 0.06	-0.14 -0.87	-0.14, -0.14 0.40, -1.34

The dispersion of surface stress is larger than that of surface energy. Specifically, the dispersion of surface stress increases after structural relaxation.

In order to investigate the statistical properties of surface energy and surface stress, we conducted analyses of 1920 surfaces whose area is equal to 1 nm^2 . The results for surface energy and surface stress are shown in Fig. 2. Both the cumulative density function and the probability density function are shown in these figures. The gradient linearity of the cumulative distribution function indicates that the dispersion shows a normal distribution. Their mean value are 1.44 J/m^2 and -0.48 N/m , their standard deviation are 0.29 J/m^2 and 0.52 N/m , their coefficient of variation are 20.1 % and 108.3 %, respectively. Since both the surface energy and the surface stress show a normal distribution, the dispersion of an area of any size can be predicted by the central limit theorem if the ergodic property is assumed. Since the number of atoms n is proportional to the surface area S , the dispersion σ can be expressed as $\sigma = \sigma_0/\sqrt{S}$, where σ_0 is 0.29 J/m and 0.52 N for surface energy and stress, respectively. Since the dispersion of surface stress is largely due to the amorphous surface structure, it is difficult to evaluate the deterministic value of surface stress using a small model as is done by the first-principles calculation, for example, when the coefficient of variation area exceeds 100 % for an area of 1 nm^2 .

Discussion

First, we here discuss how to apply the surface stress values obtained in this study to the analysis of continuum mechanics. In continuum mechanics, the Laplace pressure ΔP exerted on the solid body by the surface generation derived by Cammarata [3] as Eq. (3)

$$\Delta P = f(dA/dV) \quad (3)$$

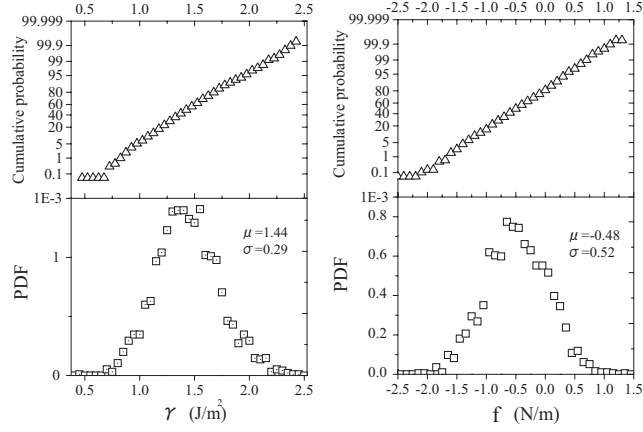


Figure 2: Cumulative (upper) and probability density (lower) function of the surface energy (left) and the surface stress (right)

In the case of the thin films with two surfaces at the top and bottom, whose thickness is t , the generated stress can be expressed as $\sigma_x = \sigma_y = 2f/t$ by the relation $\sigma_x = \sigma_y = \Delta P$. The factor of 2 arises since the thin film contains two surfaces. Although the film thickness t_{MD} cannot be determined explicitly in molecular dynamics, the equation $\sigma_{ij} = f_{ij}/t_{MD}$ holds from the surface stress definition given by Eq. (2) and $V = t_{MD}A_0$. If the film is assumed to be sufficiently thick and it is valid to regard t_{MD} as t , the stress definition obtained by molecular dynamics coincides with that of the continuum model. In this definition, σ_{ij} indicates the averaged stress over a whole film region. However, from a microscopic viewpoint, the atomic stress is concentrated in the surface region. The distribution of averaged atomistic stresses is shown in Fig. 3. It is clear that variations in stress are concentrated at the surface region with $t_{surf} \simeq 0.4$ nm width. Therefore, it follows that initial stress, $\sigma_0 = f/t_{surf}$, is generated at the surface t_{surf} region.

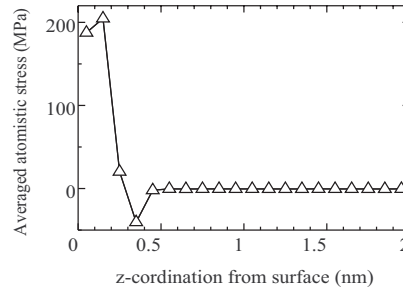


Figure 3: The distribution of atomistic stress variation

Assuming that an amorphous silicon is an isotropic body, the strain ε caused by surface stress f can be expressed using elastic theory as:

$$\varepsilon = \frac{1-\nu}{Et} f \quad (4)$$

where E is the Young modulus, and ν is a Poisson's ratio. However for an atomic system, Eq. (4) cannot be applied since the elastic property varies by the effect of surface. The strain calculated in molecular dynamics can be expressed as Eq. (5) using the surface elastic constant d_{ijkl}^{surf} (defined below) and surface stress.

$$\epsilon_{ij}^{MD} = (d_{ijkl}^{surf})^{-1} f_{ij}, \quad d_{ijkl}^{surf} = \frac{1}{A_0} \left. \frac{d^2 E^{surf}}{d\epsilon_{ij} d\epsilon_{kl}} \right|_{\epsilon=0} \quad (i, j, k, l = 1, 2) \quad (5)$$

Noted that d_{ijkl}^{surf} has no component of the z -direction; $\sigma_z = \tau_{xz} = \tau_{yz} \equiv 0$. Under this atomic system, the displacement of the z -direction is included in the internal displacement[11]. Therefore, d_{ijkl}^{surf} may refer to the elastic constants under plane stress conditions. In order to investigate the difference between the strain evaluated by Eq. (4) and (5), the elastic constants for the bulk model and the surface elastic constants for the thin film model were calculated by molecular dynamics using the method proposed by Izumi et al.[11]. The calculated model is the 1400-atom model with a thickness of 3.8 nm. The results are shown in Table. 2. Strain is obtained by substituting each elastic constant into Eq. (4) or (5). The results are shown in Table. 3. These results lead us to conclude that continuum approximation can be established in such a thin film.

Table 2: Elastic constants C_{ij} [GPa] and sur- Table 3: Surface stress f and the strain in-
face elastic constants d_{ij} [N/m] of amorphous duced by surface stress. $\epsilon_{elastic}$ is evaluated
silicon (using Voight matrix notation) by elastic theory, ϵ_{MD} is evaluated by MD.

C_{11}	C_{12}	C_{44}	d_{11}	d_{12}	d_{44}	f (N/m)	$\epsilon_{elastic}$	ϵ_{MD}
143.8	64.3	37.7	405.3	119.4	139.6	-0.28	0.99×10^{-3}	1.07×10^{-3}

Next, we discuss the effects of surface relaxation. The relaxed surface stress of the Si(001)(1×1) surface is significantly different from that of the Si(001)(2×1) surface, even though both non-relaxed surfaces show the same stress values. Only the reconstruction in the z -direction has occurred in the case of Si(001)(1×1), while dimer reconstruction has also occurred in the case of Si(001)(2×1). On the other hand, the relaxed surface stress includes not only the effect of the elastic deformation to the z -direction but also the effect of surface bond reconstruction. We investigate the effects of surface reconstruction by estimating the contribution of elastic deformation.

In the process of generation of surface stress, the stress of the non-relaxed surface is generated due to the creation of the surface without changing the atomic position. After elastic deformation to the z -direction and the reconstruction of the surface atoms, the system reaches a state of the equilibrium, namely $\sigma_z = 0$. At that time, in-plane (xy) stress is generated; this is the relaxed surface stress. For simplicity, we treat a thin film model with finite thickness, and apply the elastic theory to that model. If the strain at the non-relaxed state is assumed to be zero, the stress may be calculated by Eq. (6)

$$\sigma_x^0 = 2f_x^0/t, \quad \sigma_y = 2f_y^0/t, \quad \sigma_z^0 = 2f_z^0/t \quad (6)$$

Due to the lack of relaxation to the z -direction, the stress σ_z^0 is generated. After relaxation, the strain of the x and y directions is unchanged and the stress of the z -direction becomes zero. The

relaxed surface stresses accompanied only by elastic deformation f_x^e and f_y^e may be shown below:

$$f_x^e = f_x^0 - \frac{C_{13}}{C_{33}} f_z^0, \quad f_y^e = f_y^0 - \frac{C_{23}}{C_{33}} f_z^0 \quad (7)$$

f_x^e and f_y^e are calculated for three thin film samples with a thickness of 8.2 nm. In this calculation, we use the elastic constants obtained by the molecular dynamics calculation for the bulk amorphous silicon. $f^0=0.29\pm0.05$ N/m, $f^e=-0.043\pm0.055$ N/m, and $f=-0.54\pm0.05$ N/m are the results obtained, where f^0 is the non-relaxed surface stress and f is the relaxed surface stress. The contribution of elastic deformation during surface stress generation can be estimated at $f^e - f^0=-0.33\pm0.01$ N/m, and that of the surface reconstruction at $f - f^e=-0.49\pm0.02$ N/m. This result leads to the conclusion that the effect of reconstruction is larger than that of elastic deformation in the case of amorphous silicon. The same procedure was also carried out on c-Si(1×1). In this case, the contribution of elastic deformation was found to be -0.53 N/m and that of the reconstruction, -0.20 N/m. The contribution of elastic deformation is comparatively larger than that of amorphous silicon since no large reconstruction such as dimerization has taken place.

Conclusions

We have evaluated the statistical properties of the surface energy and the surface stress of amorphous silicon by using molecular dynamics. The results may be summarized as follows. We have obtained surface energy and surface stress values of amorphous silicon of 1.44 ± 0.03 J/m² and -0.48 ± 0.06 N/m, respectively. Since the dispersion of the surface energy and stress of amorphous silicon shows a normal distribution, that of an area of any size can be predicted by the central limit theory. The coefficient of variation in an area of 1 nm² are 20.1, 108.3 %, respectively. It was determined that the dispersion of surface stress is significantly large. For the application of surface stress to continuum mechanics. The surface stress can be treated as the initial stress generated in a surface region of a thickness of about 0.4 nm. The surface stress is strongly dependent on the reconstruction of the surface atoms. The contribution of surface reconstruction of amorphous silicon is larger than that of Si(1×1).

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