

A METHOD FOR CALCULATING SURFACE STRESS AND ELASTIC CONSTANTS BY MOLECULAR DYNAMICS

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Abstract

For nano-scale thin film, effects of surface and interface, which can be ignored on a macro scale, become important. For example, surface energy and stress are key parameters for predicting the intrinsic stress of thin films. Several researchers have reported that the elastic constants of thin films are different from those of bulks. We have recently proposed new definitions and calculation methods regarding surface stress and elastic constants for thin films by extending Martin's method, which is useful for obtaining the internal displacement and elastic constants within the framework of the molecular dynamics method. We applied our method to nano-scale thin films of crystal and amorphous silicon. The effects of surface reconstructions and the width of the surface are also investigated.

Keywords: Molecular Dynamics, Elastic constants, Surface Energy, Surface Stress

1 Introduction

The films used in the manufacture of semiconductors are less than 10 nm thick. At this thickness, the effects of surface and interface, which can be ignored on a macro scale, become important. For example, surface (interface) energy and stress are key parameters for predicting the intrinsic stress of thin films, though the stress depends also on the microstructures and growth mode at atomic level[1][2]. However, it is difficult to obtain values of surface energy and surface stress experimentally. Therefore, numerical evaluation by molecular simulation has been attempted. In addition, several researchers have reported that the elastic properties (e.g. Young module) of thin films are different from those of bulks[3][4]. In particular, the elastic properties of films with thickness in the range of several nm may exceed the range of continuum approximation. Therefore, it has become very important to investigate the limit of continuum approximation and to predict unique phe-

nomena in that thickness range. In calculating the elastic properties of inhomogeneous surface structures, the effect of internal displacement, which is non-linear atomic displacement in response to deformation, must be taken into account. We have recently proposed new definitions and calculation methods regarding surface stress and surface elastic constants for thin films with free surfaces through an extension of Martin's method[5][6]. This method is useful for obtaining the internal displacement and elastic constants within the framework of the molecular dynamics. We applied our method to nano-scale thin films of crystal and amorphous silicon. In order to investigate the depth of the surface effect, the local atomic elastic constants are newly defined. Those effects on the elastic properties of whole thin films are also discussed.

2 The definitions and calculation methods of surface energy, surface stress and surface elastic constants

Definition of surface

In order to define the surface of a molecular dynamics system, we prepared a thin film model with a free boundary condition for the z-direction and two periodic boundary conditions for the x- and y-directions as shown in Fig. 1. Therefore, the evaluation area is made up of two surfaces that face each other. The film must be enough thick to prevent interference of these two surfaces. It should be noted that the surface reconstructions greatly influence the surface properties.

Definition of strain

Since the z-direction is not subject to a periodic boundary condition, the shape matrix of a MD cell must be written in Eq. (1). Therefore in-plane deformation gradient tensor is defined by

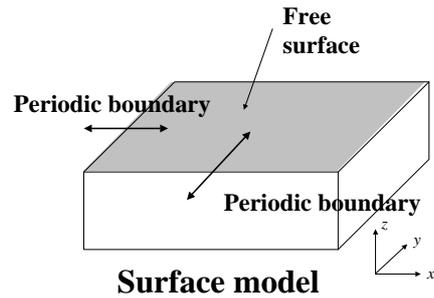


Figure:1 Surface model

$\hat{\mathbf{F}} = \hat{\mathbf{h}}\hat{\mathbf{h}}_0^{-1}$, where the subscript 0 means the state before deformation. In-plane Green-Lagrange strain $\hat{\boldsymbol{\eta}}$ can be written in Eq. (2).

$$\hat{\mathbf{h}} = \begin{pmatrix} h_{11} & h_{12} \\ h_{12} & h_{22} \end{pmatrix} \quad (1)$$

$$\hat{\boldsymbol{\eta}} = \frac{1}{2}(\hat{\mathbf{F}}^t \hat{\mathbf{F}} - \hat{\mathbf{I}}) = \frac{1}{2}(\hat{\mathbf{h}}_0^t \hat{\mathbf{G}} \hat{\mathbf{h}}_0^{-1} - \hat{\mathbf{I}}), \quad (\hat{\mathbf{G}} = \hat{\mathbf{h}}^t \hat{\mathbf{h}}) \quad (2)$$

The definitions are represented formally by three-dimensional notations, i.e. Eq. (3).

$$\hat{\mathbf{F}} = \begin{pmatrix} \hat{F}_{11} & \hat{F}_{12} & 0 \\ \hat{F}_{21} & \hat{F}_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{\boldsymbol{\eta}} = \begin{pmatrix} \hat{\eta}_{11} & \hat{\eta}_{12} & 0 \\ \hat{\eta}_{21} & \hat{\eta}_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (3)$$

Definition of internal displacement vector

Although in the elastic theory the displacements of material points become linear to a deformation, this is not the case with atomic displacements. In an atomic system, each atom moves to its most stable point in response to a deformation. This difference, between the displacement of continuum body approximation and that of the atoms, is called internal displacement.

Distance vector $\mathbf{r}^{\alpha\beta}$ between atoms α and β after a deformation can be written by the sum of the homogeneous de-

formation term (the first term on the right-hand side of Eq. (4)) and the relative displacement term (the second term), where the subscript 0 symbolizes the state before deformation.

$$\mathbf{r}^{\alpha\beta} = \hat{\mathbf{F}} \mathbf{r}_0^{\alpha\beta} + \mathbf{u}^\beta - \mathbf{u}^\alpha. \quad (4)$$

Now internal displacement vector is newly defined by $\hat{\boldsymbol{\xi}}^\alpha = \hat{\mathbf{F}}^t \mathbf{u}^\alpha$ as a rotational invariant variable. By using this definition, rotational invariant distance $s^{\alpha\beta} = (\mathbf{r}^{\alpha\beta})^t \mathbf{r}^{\alpha\beta}$ can be represented as follows:

$$\begin{aligned} s^{\alpha\beta} &= (\mathbf{r}_0^{\alpha\beta})^t (2\hat{\boldsymbol{\eta}} + \mathbf{I}) \mathbf{r}_0^{\alpha\beta} + 2(\hat{\boldsymbol{\xi}}^\beta - \hat{\boldsymbol{\xi}}^\alpha) \mathbf{r}_0^{\alpha\beta} \\ &+ (\hat{\boldsymbol{\xi}}^\beta - \hat{\boldsymbol{\xi}}^\alpha) (2\hat{\boldsymbol{\eta}} + \mathbf{I})^{-1} (\hat{\boldsymbol{\xi}}^\beta - \hat{\boldsymbol{\xi}}^\alpha). \end{aligned} \quad (5)$$

From Eq. (5), the variation in the interatomic distance in response to the deformation $\hat{\mathbf{F}}$ (averaged strain $\hat{\boldsymbol{\eta}}$) can be derived.

It should be noted that displacements in the z-direction are included in the internal displacement vector $\hat{\boldsymbol{\xi}}^\alpha$.

Definition of surface energy

Surface energy γ is the energy variation per unit area due to the surface creation. It is defined by Eq. (6). E^{surf} and E^{bulk} are the energy of the system with and without the surface, respectively. The latter value must be estimated separately by a bulk model. A is the surface area of two free surfaces.

The strain is defined so that the cell size in the zero-strain state is equal to that of the zero-stress state of a bulk; that is, the strain corresponding to the lattice parameter at a bulk stress of zero is defined as zero.

$$\begin{aligned} \gamma(\hat{\boldsymbol{\eta}}) &= \frac{1}{A(\hat{\boldsymbol{\eta}})} (E^{surf}(\hat{\boldsymbol{\eta}}) - E^{bulk}(\hat{\boldsymbol{\eta}})) \\ &= \frac{E^\gamma(\hat{\boldsymbol{\eta}})}{A(\hat{\boldsymbol{\eta}})} \end{aligned} \quad (6)$$

Definition of surface stress

Surface stress is the variation in total surface energy (E^γ) per unit area with respect to the strain $\hat{\eta}_{ij}$. This variation corresponds to the stress generated by creation of the surface.

$$\begin{aligned} f_{ij}(\hat{\boldsymbol{\eta}}) &= \frac{1}{A_0} \left. \frac{d(A(\hat{\boldsymbol{\eta}})\gamma(\hat{\boldsymbol{\eta}}))}{d\hat{\eta}_{ij}} \right|_{\hat{\boldsymbol{\eta}}'=0, \hat{\boldsymbol{\xi}}'=0}, \\ &(i, j = 1, 2) \end{aligned} \quad (7)$$

$\hat{\boldsymbol{\eta}}'$ means that all components except for the differentiating component are set to zero. Unlike thin-film stress, surface stress does not depend on thickness, since the surface effect is not divided by volume but by surface area as in Eq. (7). Therefore, it can be said that surface stress is an intrinsic property of the surface.

If $\gamma(\varepsilon)$ is not dependent on the strain, which is the case with liquid,

$$f_{ij}(\hat{\boldsymbol{\eta}}) = \frac{1}{A_0} \cdot A_0 \delta_{ij} \gamma(\hat{\boldsymbol{\eta}}) = \gamma(\hat{\boldsymbol{\eta}}) \delta_{ij}. \quad (8)$$

If $\gamma(\varepsilon)$ is dependent on the strain, which is the case with solid,

$$f_{ij}(\hat{\boldsymbol{\eta}}) = \gamma(\hat{\boldsymbol{\eta}}) \delta_{ij} + \frac{A(\hat{\boldsymbol{\eta}})}{A_0} \frac{d\gamma(\hat{\boldsymbol{\eta}})}{d\hat{\eta}_{ij}}. \quad (9)$$

The second term is the characteristic term for a solid only.

When we apply this definition to molecular dynamics, Eq. (10) is obtained by using E^γ .

$$\begin{aligned} f_{ij}(\hat{\boldsymbol{\eta}}) &= \frac{1}{A_0} \left. \frac{dE^\gamma}{d\hat{\eta}_{ij}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}'=0} = \frac{1}{A_0} \left. \frac{\partial E^\gamma}{\partial \hat{\eta}_{ij}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}'=0} \\ &= \frac{1}{A_0} \left(\left. \frac{\partial E^{surf}(\hat{\boldsymbol{\eta}})}{\partial \hat{\eta}_{ij}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}'=0} \right. \\ &\quad \left. - \left. \frac{\partial E^{bulk}(\hat{\boldsymbol{\eta}})}{\partial \hat{\eta}_{ij}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}'=0} \right) \\ &= f_{ij}^{surf}(\hat{\boldsymbol{\eta}}) - f_{ij}^{bulk}(\hat{\boldsymbol{\eta}}) \quad (i, j = 1, 2). \end{aligned} \quad (10)$$

Since the stress does not depend on the internal displacement[5], total differentiations can be replaced by partial differentiations.

$f_{ij}^{bulk}(\hat{\boldsymbol{\eta}})$ must be estimated separately by the bulk model. In general, the stress tensor of the bulk model is defined by using the shape matrix shown below.

$$\mathbf{h} = \begin{pmatrix} h_{11} & h_{12} & h_{13} \\ h_{12} & h_{22} & h_{23} \\ h_{13} & h_{23} & h_{33} \end{pmatrix} \quad (11)$$

A different strain tensor $\boldsymbol{\eta}$ and a different internal displacement vector $\boldsymbol{\xi}^\alpha$ are defined by using \mathbf{h} . However, since the stress is not dependent on the internal displacement, the definition by using $\boldsymbol{\eta}$ and that by using $\hat{\boldsymbol{\eta}}$ become equivalent to each other in the case of $i, j = 1, 2$.

$$\begin{aligned} f_{ij}^{bulk}(\hat{\boldsymbol{\eta}}) &= \frac{1}{A_0} \left. \frac{\partial E^{bulk}}{\partial \hat{\eta}_{ij}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0}, (i, j = 1, 2) \\ &= \frac{1}{A_0} \left. \frac{\partial E^{bulk}}{\partial \eta_{ij}} \right|_{\boldsymbol{\eta}', \boldsymbol{\xi}' = 0} \end{aligned} \quad (12)$$

Therefore, the stress tensor can be defined by Eq. (13), where we assume that the volume is $V_0 = A_0 L_z / 2$ and m indicates *bulk* or *surf*.

$$\sigma_{ij}^m(\hat{\boldsymbol{\eta}}) = \frac{1}{V_0} \left. \frac{dE^m}{d\hat{\eta}_{ij}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0} = 2f_{ij}^m(\hat{\boldsymbol{\eta}})/L_z \quad (13)$$

Definition of surface elastic constants

Surface elastic constants are defined as second-order derivatives of surface energy with respect to the strain $\hat{\eta}_{ij}$, which represents the variation in elastic properties due to surface creation.

$$\begin{aligned} d_{ijkl}(\hat{\boldsymbol{\eta}}) &= \frac{1}{A_0} \left. \frac{d^2(A(\hat{\boldsymbol{\eta}})\gamma(\hat{\boldsymbol{\eta}}))}{d\hat{\eta}_{ij}d\hat{\eta}_{kl}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0} \\ &= \frac{1}{A_0} \left(\left. \frac{d^2 E^{surf}(\hat{\boldsymbol{\eta}})}{d\hat{\eta}_{ij}d\hat{\eta}_{kl}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0} \right) \end{aligned}$$

$$\begin{aligned} & - \left. \frac{d^2 E^{bulk}(\hat{\boldsymbol{\eta}})}{d\hat{\eta}_{ij}d\hat{\eta}_{kl}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0} \\ & = d_{ijkl}^{surf}(\hat{\boldsymbol{\eta}}) - d_{ijkl}^{bulk}(\hat{\boldsymbol{\eta}}) \end{aligned} \quad (14)$$

$$d_{ijkl}^{surf} = (d_{ijkl}^0)^{surf} + (d_{ijkl}^*)^{surf} \quad (15)$$

$$(d_{ijkl}^*)^{surf} = -\frac{1}{A_0} D_{ijm}^\alpha g_{mn}^{\alpha\beta} D_{klm}^\beta \quad (16)$$

$$(d_{ijkl}^0)^{surf} = \frac{1}{A_0} \left. \frac{\partial^2 E^{surf}}{\partial \hat{\eta}_{ij} \partial \hat{\eta}_{kl}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0} \quad (17)$$

$$D_{ijk}^\alpha = \left. \frac{\partial^2 E^{surf}}{\partial \hat{\eta}_{ij} \partial \hat{\xi}_k^\alpha} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0} \quad (18)$$

$$\begin{aligned} E_{ij}^{\alpha\beta} &= \left. \frac{\partial^2 E^{surf}}{\partial \hat{\xi}_i^\alpha \partial \hat{\xi}_j^\beta} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0} \\ &; g_{ij}^{\alpha\beta} E_{jk}^{\beta\gamma} = \delta^{\alpha\gamma} \delta_{ik} \end{aligned} \quad (19)$$

$(d_{ijkl}^0)^{surf}$ and $(d_{ijkl}^*)^{surf}$ are referred to as local and relaxation term, respectively. D_{ijk}^α and $E_{ij}^{\alpha\beta}$ correspond to the piezoelectric constants and the force constants between atoms, respectively. Since the elastic constants depend on the internal displacement, and since different definitions of strain and internal displacement are used between the bulk and surface models, d_{ijkl}^{bulk}/L_z is not equal to the usual elastic constants, unlike the case with stress.

$$\left. \frac{d^2 E^{bulk}}{d\hat{\eta}_{ij}d\hat{\eta}_{kl}} \right|_{\hat{\boldsymbol{\eta}}', \hat{\boldsymbol{\xi}}' = 0} \neq \left. \frac{d^2 E^{bulk}}{d\eta_{ij}d\eta_{kl}} \right|_{\boldsymbol{\eta}', \boldsymbol{\xi}' = 0} \quad (20)$$

$$d_{ijkl}^{bulk} \neq \frac{L_z}{2} C_{ijkl},$$

$$\left(C_{ijkl} = \frac{1}{V_0} \left. \frac{d^2 E^{bulk}}{d\eta_{ij}d\eta_{kl}} \right|_{\boldsymbol{\eta}', \boldsymbol{\xi}' = 0} \right) \quad (21)$$

d_{ijkl}^{bulk} corresponds to the elastic constants under the two-dimensional plane-stress condition ($\sigma_z = \gamma_{xz} = \gamma_{yz} \equiv 0$).

For example, d_{ijkl}^{bulk} can be written by Eq. (22)-(25) in the orthotropic elastic body, where the Voigt notation is used.

$$d_{11}^{bulk} = L_z \left(C_{11} - \frac{C_{13}^2}{C_{33}} \right) \quad (22)$$

$$d_{22}^{bulk} = L_z \left(C_{22} - \frac{C_{23}^2}{C_{33}} \right) \quad (23)$$

$$d_{12}^{bulk} = L_z \left(C_{12} - \frac{C_{12}C_{13}}{C_{33}} \right) \quad (24)$$

$$d_{44}^{bulk} = L_z C_{44} \quad (25)$$

From the definition of Eq. (14), it is shown that the surface elastic constants are coefficients between surface stress f_{ij} and strain $\hat{\eta}_{kl}$ as shown in Eq.(26). $f_{ij}(\mathbf{0})$ is the surface stress at the zero strain state, which originates in the fact that the strain is defined on the basis of the state of the bulk.

$$d_{ijkl}(\hat{\eta})\hat{\eta}_{kl} = f_{ij}(\hat{\eta}) - f_{ij}(\mathbf{0}) \quad (26)$$

3 Results

Analysis condition

We applied our method to nano-scale thin films of crystal and amorphous silicon. Two kinds of crystal surfaces, i.e., (100)1×1 and (100)2×1, and two kinds of amorphous surfaces, i.e., relaxed and well-annealed, are prepared. The Tersoff potential is used to model the silicon[7].

For the amorphous model, we prepared a bulk model including 1000 atoms and with overall size of 2.7×2.7×2.7 nm. First the structures of the bulk amorphous silicon were produced by a melt-quench method. Then the structures are annealed at 1600K for 10 ns. The surfaces are formed by removing the periodic boundary condition of the z-direction. After the surfaces are created, the systems are relaxed by the conjugated gradient

method (relaxed surface) or by thermal annealing for 4ns at 1200K and 2ns at 800K (well-annealed surface). This recipe is determined so that the state of the bulk does not change by annealing.

Three samples are produced.

Surface energy, surface stress and surface elastic constants

The surface energy γ , surface stress f (in-plane f_{11} and f_{22}) and surface elastic constants d_{IJ} are shown in Tables 1 and 2.

Table:1 Surface energy γ (J/m²) and surface stress f (N/m) of the surface of crystal silicon and amorphous silicon, whose evaluation area is 14.6 nm². The x -direction of the (2×1) surface model corresponds to the dimer-bonding

	γ	f_{11}, f_{22}
(100) 1×1	2.27	-0.88
(100) 2×1	1.48	0.40, -1.34
a-Si(relaxed)	1.62±0.06	-0.50±0.19
a-Si(well-ann.)	1.07±0.06	1.38±0.19

The surface energy of crystal decreases from 2.27 J/m² to 1.48 due to the (2×1) reconstruction. The compressive in-plane surface stress also decreases, from -0.88 to -0.50 N/m. The well-annealed amorphous surface has the lowest surface energy, 1.07 J/m², and a large tensile surface stress, 1.38 N/m. These variations are caused by a large reconstruction of the amorphous surface. The coordination number and ring statistics are shown in Tables. 3 and 4, respectively. From the comparison of the relaxed amorphous surface with the well-annealed one, we can see that annealing resulted in the disappearance of the 2-coordination number and the increase of the 4-coordination number. Increases in the number of six- and seven-membered rings are also observed. It is thought that the strong structures of the bond network are constructed by the surface

Table:2 Surface elastic constants d_{IJ} (N/m) of the surface of crystal silicon and amorphous silicon

	d_{11}, d_{22}	d_{12}	d_{44}
(100) 1×1	-8.1	0.28	-3.6
(100) 2×1	-17.8, -0.7	-0.55	-0.40
a-Si(relaxed)	-11.2 ± 2.3	-5.7 ± 1.8	-2.4 ± 0.5
a-Si(well-annealed)	-7.1 ± 4.2	-4.9 ± 0.4	-1.2 ± 2.7

reconstruction, and that those effects influence the surface properties greatly.

While the coordination number of a well-annealed amorphous surface is almost the same as that of the crystal silicon surface (100)(2×1), the ring statistics show a different tendency, i.e. the amorphous surface has a larger number of five- and seven-membered rings. This reflects the difference in the bond network between amorphous and crystal surfaces.

The negative surface elastic constants also decreased due to the surface reconstruction. This indicates that the elastic properties of thin films approach those of bulks.

4 Discussion

Distribution of atomic elastic constants

In order to investigate the depth of the surface effect, the local atomic elastic constants, $(d_{ijkl}^{0\alpha})^{surf}$, are newly defined by Eq. (27), which expresses qualitatively the contribution of the local effect to the whole system. Therefore, its definition is intrinsically different from $(d_{ijkl}^0)^{surf}$.

$$\begin{aligned}
 d_{ijkl}^{0\alpha} &= (d_{ijkl}^{0\alpha})^{surf} - (d_{ijkl}^{0\alpha})^{bulk} \\
 &= \frac{A_0}{A_0^\alpha} \sum_{\beta} \frac{\partial f_{ij}^{surf}}{\partial r^{\alpha\beta}} \frac{\partial r^{\alpha\beta}}{\partial \eta_{ij}} - (d_{ijkl}^{0\alpha})^{bulk}, \\
 &\quad \left(\frac{1}{N} \sum_{\alpha} d_{ijkl}^{0\alpha} = d_{ijkl}^0 \right) \quad (27)
 \end{aligned}$$

N and A_0^α are the number of atoms and the surface area per atom, respectively.

The distributions of $d_{11}^{0\alpha}$ and $d_{44}^{0\alpha}$ along the direction of thickness are shown in Fig. 2 and 3 for (100) 2×1 and relaxed a-Si surfaces. Both ends of the x-axis correspond to the surface area.

In contrast to the continuum approximation, the elastic constants of an atomic system show not a homogeneous distribution but an inhomogeneous one. The scattering region of atomic elastic constants reaches about four atomic layers. Therefore, negative (soft) surface elastic constants are generated mainly within three or four atomic layers from the surface, which corresponds to a width of 0.2-0.5 [nm].

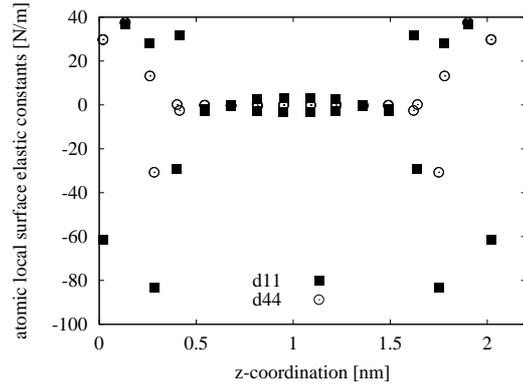


Figure:2 Distribution of atomic local elastic constants along the z-direction. (001) 2×1 surface model

Dependence of surface elastic constants on the thickness

The dependence of the surface stress and that of the surface elastic constants

Table:3 Ratio of the coordination number within 5.5nm from the surface. The standard deviation of amorphous results is in the range of 0 to 2 %

	N_2	N_3	N_4	N_5	N_{ave}
(100) 1×1	22.2	0	77.8	0	3.56
(100) 2×1	0	22.2	77.8	0	3.78
Crystal(Bulk)	0	0	100	0	4
a-Si(relaxed)	8.8	20.7	65.9	3.8	3.63
a-Si(well-annealed)	0.0	22.6	74.8	2.5	3.79
a-Si(Bulk)	0	0.1	96.2	3.7	4.03

Table:4 Ring statistics within 5.5nm from surface

	R_3	R_4	R_5	R_6	R_7
(100) 1×1	0	0	0	1.33	0
(100) 2×1	0	0	0.22	1.44	0.22
Crystal(Bulk)	0	0	0	2	0
a-Si(relaxed)	0.00	0.03	0.32	0.69	0.66
a-Si(annealed)	0.00	0.03	0.40	0.81	0.80
a-Si(Bulk)	0.00	0.03	0.40	1.03	1.03

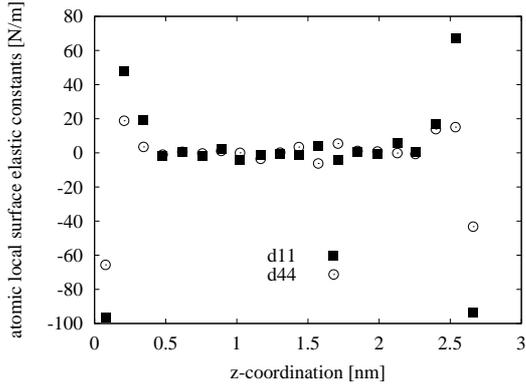


Figure:3 Distribution of atomic local elastic constants along the z-direction. Relaxed amorphous surface model

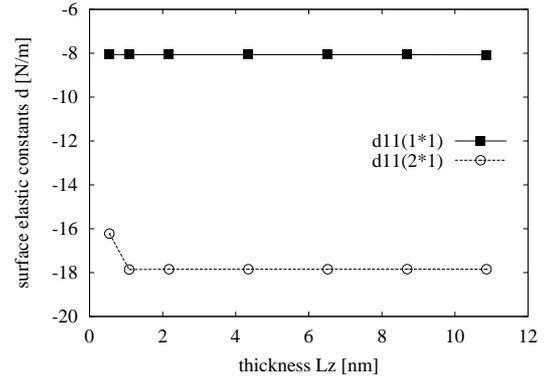


Figure:4 Surface elastic constants d_{11} as a function of film thickness L_z for c-Si surface.

Deviation from the continuum approximation

on the thickness have been investigated. The results of (100)1×1 and (100)2×1 surfaces are shown in Fig. 4 for d_{11} .

The values of elastic constants d_{11} are not dependent on the film thickness. Below 1nm thickness, a small variation of d_{11} appears. These are caused by the interference of surfaces, since the surface effect reaches about 0.5nm as shown in Fig. 2.

Since the surface elastic constants include only the surface effect and do not depend on the film thickness, the elastic constants of the whole thin film gradually approach those of bulks as the thickness increases. Therefore, the in-plane strain of a thin film caused by the same surface stress decreases as the thickness decreases, due to the softening effect of the surface elastic constants. In the isotropic case, in-plane strain $\hat{\eta}^{film}$ caused by surface stress at the zero-

strain state is written by Eq. (28) from $f_{ij}^{surf} = 0$.

$$\hat{\eta}^{film} = \frac{f_{11}}{d_{11}^{surf} + d_{12}^{surf}} \quad (28)$$

On the other hand, if the film is approximated by a continuum body, in-plane strain $\hat{\eta}^{bulk}$ can be written by replacing d^{surf} into d^{bulk} in Eq. (28). Therefore, Eq. (28) can be written in simple form by using $d_{ij}^{surf} = d_{ij}^{bulk} + d_{ij}$ and Eq. (22)-(25).

$$\hat{\eta}^{film} = \frac{f}{d_{11} + d_{12} + L_z \frac{(C_{11} + 2C_{12})(C_{11} - C_{12})}{C_{11}}} \quad (29)$$

The deviation of $\hat{\eta}^{film}$ from $\hat{\eta}^{bulk}$ can be written by film thickness L_z and softening parameter C^* which we have newly defined.

$$\text{dev} = \frac{\hat{\eta}^{film} - \hat{\eta}^{bulk}}{\hat{\eta}^{bulk}} = -\frac{1}{1 + L_z C^*},$$

$$C^* = \frac{(C_{11} + 2C_{12})(C_{11} - C_{12})}{C_{11}(d_{11} + d_{12})}. \quad (30)$$

As the thickness increases, the deviation approaches zero. The curve of a well-annealed surface of amorphous silicon is shown in Fig. 5 as a function of thickness L_z . The deviation from the continuum approximation becomes less than 5% when the thickness exceeds approximately 5nm. These results lead us to conclude that continuum approximation can be established in such a thin film.

5 Conclusions

We have proposed new definitions and calculation methods regarding surface stress and elastic constants for thin films by extending Martin's method, which is useful for obtaining the internal displacement and elastic constants within

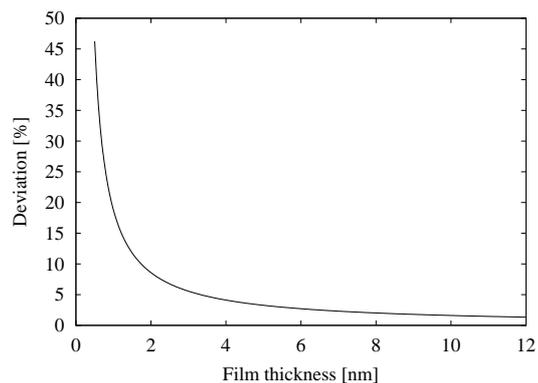


Figure:5 Deviation of in-plane strain as a function of film thickness (well-annealed surface of amorphous silicon)

the framework of the molecular dynamics method. We applied our method to nano-scale thin films of crystal and amorphous silicon. The effects of surface reconstructions were also investigated. The well-annealed surface has remarkably different properties compared with the relaxed surface. The width of the surface is also discussed in terms of newly defined atomic-level elastic properties. It is found that the width of the surface is approximately 0.5nm.

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