

Interplay between quantum size effect and strain effect on growth of nanoscale metal thin filmsMiao Liu,¹ Yong Han,^{1,*} Lin Tang,² Jin-Feng Jia,² Qi-Kun Xue,² and Feng Liu^{1,†}¹*Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA*²*Department of Physics, Tsinghua University, Beijing 100084, China*

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We develop a theoretical framework to investigate the interplay between the quantum size effect (QSE) and strain effect on the stability of metal nanofilms. The QSE and strain effect are shown to be coupled through the concept of quantum electronic stress. First-principles calculations reveal large quantum oscillations in the surface stress of metal nanofilms as a function of film thickness, which adds extrinsically additional strain-coupled quantum oscillations to the surface energy of *strained* metal nanofilms. Our theory enables a quantitative estimation of the amount of strain in experimental samples, and suggests strain to be an important factor contributing to the discrepancies between the existing theories and experiments.

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When the thickness of a metal film is reduced to the range of the electron Fermi wavelength, quantum confinement becomes prominent to form discrete quantum well states, giving rise to various manifestations of the quantum size effect (QSE).¹ In particular, the QSE has been shown to be a dominant factor in the growth of metal nanofilms on semiconductor substrates^{1–5} in the so-called electronic growth regime.² On the other hand, the strain effect is ubiquitous in heteroepitaxial growth of semiconductor and metal thin films.^{6,7} A few recent studies^{8–12} have considered both effects on metal thin film growth. One thermodynamic theory⁸ studied both effects on film stability, and two kinetic models^{10,11} assumed growth parameters to be dependent on island height and radius due to the QSE and strain effect. However, majority studies have focused on one effect while neglecting the other, and those few studies which considered both effects have been generally limited to treating them as two independent additive effects. This is mostly because fundamentally no theory is available to assess how the QSE may change the stress state of the film, and conversely how strain may alter the QSE. Therefore, it is very important to establish a theoretical framework that underlies the QSE on surface stress that in turn underlies the interplay between the QSE and strain effect.

The Pb(111) film grown on a Si(111) substrate has been extensively studied as a model system for QSE [Refs. 3–5, 13, 14]. The almost perfect matching between the Pb Fermi wavelength and its interlayer spacing in the (111) direction gives rise to two striking QSE features in Pb film: the odd-even oscillations and beating patterns exhibited in many properties, such as surface energy and stability. These two main features have been agreed upon by all theoretical and experimental studies.^{3–5, 13, 14} However, there remain some outstanding discrepancies. Oscillation patterns may vary slightly from one experimental sample to another.^{13–16} First-principles calculations⁴ predicted that the odd-even oscillations in a surface energy essentially die out at a thickness of ~ 20 monolayers (MLs), while experiments, in contrast, have seen the large oscillations sustained even beyond 30 MLs.^{13, 14} One origin of the discrepancies was attributed to Pb/Si interface that causes a phase shift in the oscillation patterns,³ but the strain effect has been mostly overlooked so far.

Because of the large lattice mismatch, the Pb(111) film tends to grow on a Si(111) substrate by adopting a 10-to-9 epitaxial

relation to minimize interfacial misfit strain.^{17, 18} Even so, Pb film can still experience up to $\pm 3\%$ strain depending on the film orientation relative to Si surface.¹⁷ The measurement of interlayer spacing by X-ray diffraction¹³ suggested that the strain in Pb film is small based on the bulk Poisson ratio, but the actual amount of in-plane strain remains uncertain, because the ultrathin film may not follow the bulk Poisson ratio, especially in the presence of the QSE that modifies the interlayer spacing. Overall, the strain effect has not been studied adequately in relation with the QSE, because of the lack of theory underlying their relationship and because the direct measurement of strain in the film is very difficult.

In this paper, we develop a general theory underlying the fundamental relationship between the QSE and strain effect in the formulation of surface energy through the concept of “quantum electronic stress,”¹⁹ i.e., the additional surface stress oscillations induced by the QSE. Using first-principles density functional theory (DFT) calculations, we reveal large quantum oscillations in the surface stress of Pb(111) films as a function of thickness, which adds extrinsically additional strain-mediated quantum oscillations to surface energies of the strained Pb films. Our theory enables a quantitative estimation of the amount of strain in different experimental samples from the measured stability patterns.

We first briefly introduce the concept of quantum electronic stress that gives rise to quantum oscillations of surface stress. Figure 1 illustrates the fundamental difference between the conventional mechanical surface stress and the new quantum surface stress. Consider heteroepitaxial growth of a strained island on a surface of thickness d under strain ε due to a lattice mismatch, as shown in Fig. 1(a). σ^i denotes the intrinsic nonzero surface stress of any given solid surface.^{20, 21} In addition, there is a mechanical surface stress induced by misfit strain, which can be calculated as $\sigma^M = \varepsilon Ed$ [Ref. 22], where E is an elastic constant. Then the total surface stress of the growing film is $\sigma^T = \sigma^i + \sigma^M$. In contrast, consider the heteroepitaxial growth of an unstrained metal island in the quantum growth regime with a strong QSE, as shown in Fig. 1(b). There will be no additional mechanical surface stress induced by misfit strain, but instead an additional thickness-dependent quantum surface stress [$\sigma^{QS}(d)$] induced by the QSE. Then the total surface stress of the growing film becomes $\sigma^T = \sigma^i + \sigma^{QS}$.

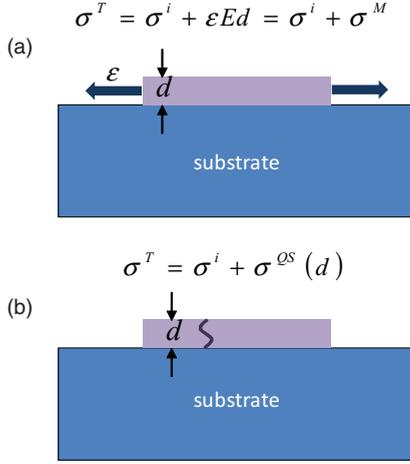


FIG. 1. (Color online) Schematic illustration to differentiate the conventional mechanical surface stress induced by misfit strain from the new quantum electronic surface stress induced by the QSE. (a) A strained film in heteroepitaxial growth, showing the mechanical surface stress. (b) An unstrained film in homoepitaxial growth, showing the quantum surface stress.

Following DFT, the total energy functional of a solid is written as

$$E[n(\vec{r}), \{\vec{R}_m\}] = E_e[n(\vec{r})] + E_{\text{ext}}[n(\vec{r}), \{\vec{R}_m\}] + E_I[\{\vec{R}_m\}]. \quad (1)$$

$E_e[n(\vec{r})]$ is the electronic energy functional of charge density $n(\vec{r})$, including kinetic and electron-electron interaction energy, $E_{\text{ext}}[n(\vec{r}), \{\vec{R}_m\}]$ is the ion-electron interaction energy, $E_I[\{\vec{R}_m\}]$ is the ion-ion interaction energy, and $\{\vec{R}_m\}$ are atomic coordinates. Consider a variation of electron density from the ground state n^0 as $n^* = n^0 + \delta n$ in the absence of strain (i.e., without any lattice deformation); a general expression for lattice stress induced by such pure electronic perturbation or excitation has been recently derived as¹⁹

$$\sigma_{ij}^{QE} = \frac{1}{V} \int_V \frac{\partial \mu}{\partial \varepsilon_{ij}} \delta n(\vec{r}) d\vec{r}, \quad (2)$$

which is called quantum electronic stress. μ is the electron chemical potential, $\partial \mu / \partial \varepsilon_{ij}$ is electron deformation potential, and ε_{ij} is strain. In a nanofilm of thickness d , the QSE induces a variation of charge density and deformation potential along the surface normal z direction. Then a special form of quantum electronic “surface” stress can be expressed as

$$\sigma_{ij}^{QS} = \frac{1}{d} \int \frac{\partial \mu}{\partial \varepsilon_{ij}}(z) \delta n(z) dz. \quad (3)$$

Note that ε_{ij} is a rank-3 or rank-2 strain tensor in Eq. (2) or (3), respectively.

We have performed DFT calculations to directly reveal quantum surface stress oscillations in Pb(111) nanofilms. Our calculations are done using VASP code²³ based on density functional theory in a plane-wave formalism. For all the freestanding Pb films and Pb film on a Si substrate from 1 to 11 MLs, the ultrasoft pseudopotential²⁴ and generalized gradient approximation are used with the Pb $5d$ orbitals included as

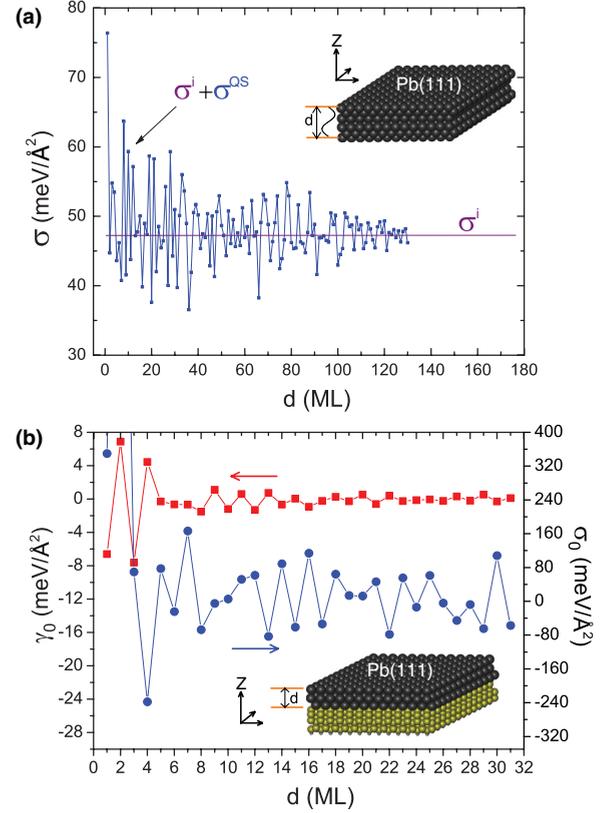


FIG. 2. (Color online) (a) Surface stress of a freestanding Pb(111) film as a function of film thickness, demonstrating the quantum surface oscillations induced by the QSE. (b) Surface energy (squares) and surface stress (dots) of a Si-supported unstrained Pb(111) film obtained from DFT calculations. The inset show schematics of film.

valence states. For thicker Pb film (12 MLs and thicker) on a Si substrate, the Perdew-Burke-Ernzerhof (PBE) potential²⁵ and generalized gradient approximation without $5d$ orbitals are used to save time. All calculations use a plane-wave cutoff of 240 eV to obtain good convergence for stresses which typically converge slower than the total energy. The Pb film is modeled by a supercell slab with the strain-free film set at the theoretical bulk lattice constant of 5.04 Å. The Si substrate was modeled using six layers of Si with the bottom two layers fixed at bulk positions and the bottom layer passivated with H. The slabs are separated by a vacuum thickness of >20 Å in the z direction, sampled by a $20 \times 20 \times 1$ mesh in k space.

Figure 2(a) shows the calculated surface stress σ , as a function of film thickness d up to 130 MLs, of the freestanding strain-free Pb(111) film. It is well known that surface energy displays an oscillatory dependence on d [Ref. 4]. What's new is that surface stress σ displays also a strong oscillatory dependence on d . In general, we may also express the surface stress as $\sigma = \sigma^i + \sigma^{QS}(d)$, where σ^i is the intrinsic surface stress of a macroscopic thick film which we are familiar with, and σ^{QS} is the new oscillating component of the quantum surface stress. The thickness dependence of the quantum surface stress is originated from the thickness dependent variation of the charge density $\delta n(z)$ and electron deformation potential induced by QSE as shown in Eq. (3). As the film

thickness increases, however, σ^{QS} will eventually diminish and σ will converge to σ^i as indicated by the decreasing oscillation magnitude with increasing thickness in Fig. 2(a) although we couldn't calculate thicker film beyond 130 MLs to show full convergence.

In experiments, Pb films are grown on semiconductor substrates, such as Si and Ge. Hence, in order to compare with experiments, we must also include the substrate and interfacial effects. Figure 2(b) shows the calculated surface energy γ_0 and surface stress σ_0 as a function of d ranging from 1 to 31 MLs of the strain-free Pb(111) film on a Si substrate (To do so, the Si substrate is strained to match the Pb lattice⁵). For either freestanding or substrate-supported Pb (111) film, we found that both the surface energy and stress show an odd-even oscillation modulated by a nine-layer beating pattern; stress σ_0 displays a larger oscillation magnitude than energy γ_0 , and stress converges much slower than energy to the macroscopic value with increasing thickness. Also, the presence of a Si substrate causes a phase shift in γ_0 and σ_0 by ~ 1 ML relative to the freestanding film.

We note that the QSE induces quantum oscillations in both surface energy and stress, but it should not affect the fundamental relation between energy, stress, and strain. The oscillating quantum surface stress provides a direct link between the QSE and strain effect on the surface energy and, hence, the stability of thin films in the quantum regime. In particular, under a given strain ε , the surface energy will have the following thickness dependence within linear elasticity

$$E(\varepsilon) = E_0(d) + A[\sigma^i + \sigma^{QS}(d)] \cdot \varepsilon. \quad (4)$$

In Eq. (4), the first term is the surface energy of an unstrained film (denoted by subscript "0") which has a thickness d dependence (quantum oscillations) due to the QSE alone. The second term is the strain induced surface energy via macroscopic surface stress, which is independent of thickness. While the third term is the strain induced surface energy via quantum surface stress, which adds extrinsically additional strain-coupled quantum oscillations to the surface energy because of the newly discovered oscillating quantum surface stress. Equation (4) enables a quantitative assessment of the interplay between the QSE and strain effect on the stability of metal nanofilms.

To verify our theoretical framework, we first calculated the surface energies of the 1% strained film as a function of thickness in comparison with the model predictions, as shown in Fig. 3. We see that the model predictions agree very well with the direct DFT results, validating our theory. Thus, using the DFT calculated surface energies and surface stresses of the "unstrained" film, we can apply our model to predict the surface energy γ of the strained film with or without substrate support.

Figures 4(a) and 4(b) show the predicted surface energies of the freestanding and Si-supported Pb(111) films strained from -3% to 3% , respectively. Strain modifies the surface energy in two important ways. First, strain enhances the QSE by increasing the odd-even oscillation magnitude in γ . This enhancement extends the QSE induced surface energy oscillations to much thicker films (the oscillation persisting beyond 30 ML with $\sim 3\%$ strain). So, strain provides one

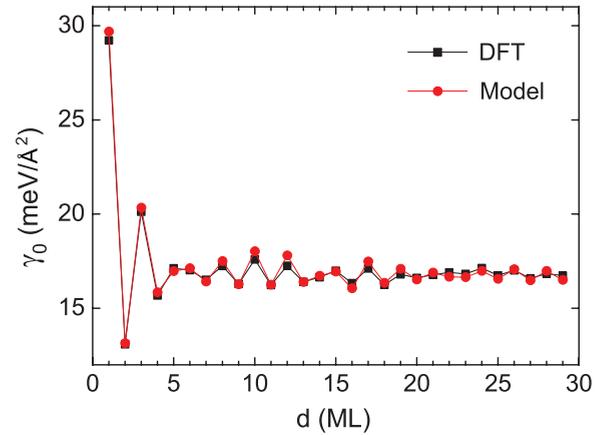


FIG. 3. (Color online) Comparison of surface energy between the model prediction and direct DFT calculation for a Pb film under 1% strain, showing excellent agreement.

possible reason for the experimentally observed stability oscillations existing in much thicker films (>30 ML)¹³ than the previous theoretical predictions (~ 20 ML).⁴ Second, because the quantum oscillations in surface stress and surface energy are phase shifted, large enough strain will change the oscillation pattern (both the odd-even and beating pattern) of the surface energy. This means that strain will alter the relative film stability of different thicknesses. For example, for the strain-free freestanding film, the 14 ML film is stable and the 15 ML is unstable; however, under 3% strain, the 14 ML becomes unstable and the 15 ML becomes stable, as shown in Fig. 4(a).

Experimentally, the observed stability patterns of Pb(111) films grown on Si(111) from different groups are in generally good agreement but with some subtle differences around the nodal points of thicknesses in the beating pattern.¹³⁻¹⁶ The reason for such a discrepancy remains unresolved, although some general argument has been made by attributing the discrepancy to a nonspherical Fermi surface²⁶ and substrate effect.^{3,8} Here, we argue that the discrepancy is partly caused by the different amount of strain in different experimental

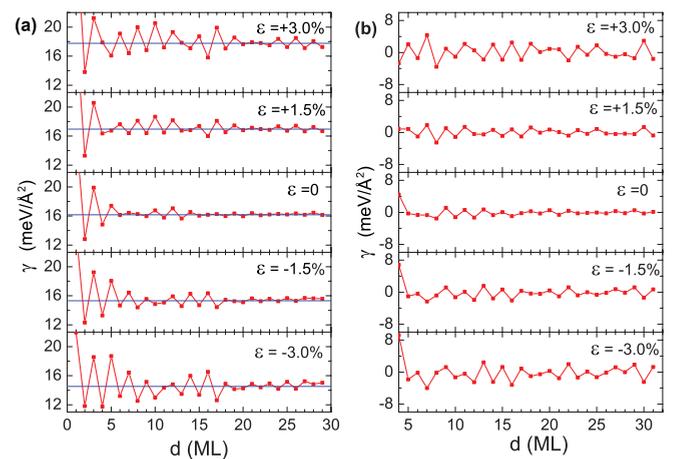


FIG. 4. (Color online) Model predicted surface energies of Pb(111) films under strain from -3% to 3% . (a) Freestanding film and (b) Si-supported film.

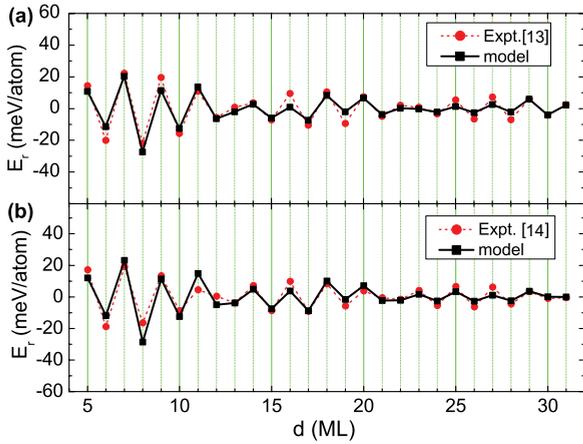


FIG. 5. (Color online) Comparison of relative surface energies of Pb(111) film on a Si substrate between the experiment (dots)^{13,14} and model prediction with the fitted strain (square).

samples. Below, we apply our model to extract the amount of strain in some experimental samples by matching the predicted stability patterns to the experiments.

Without strain, the calculated stability pattern from the Si-supported film still agrees poorly with the experiments by Czochke *et al.*¹³ and Zhang *et al.*,¹⁴ as seen by comparing Fig. 2(b) with Fig. 5. In particular, both experimental results show large odd-even oscillations from five to eight MLs (Fig. 5), while the theory shows little oscillation in this region [Fig. 2(b)] which is in the vicinity of a nodal point of the beating pattern. To resolve this discrepancy, we apply Eq. (4) to predict the stability pattern of “strained” Pb films on the Si substrate, using the calculated surface/interface energies and stresses of the unstrained film on the Si substrate. In fitting the experimental data, we assume a nonuniform strain distribution in the film that decreases linearly with the increasing film thickness,²⁷ and then treat the strain and its decay rate as fitting parameters. We obtained very good fitting results by using a linear strain profile of $1.76\% - (d - 5) \times 0.068\%$ for Czochke *et al.*’s sample¹³ and $1.80\% - (d - 5) \times 0.061\%$ for Zhang *et al.*’s sample,¹⁴ respectively, as shown in Fig. 5. Most noticeably, our model correctly predicted the large odd-even oscillations in the range 5–8 MLs as seen in the experiments. This is because there is a large oscillation in the surface stress in this range (see Fig. 2), which induces additional oscillations in the surface energy when strain is applied. The fitted strains are only slightly different in the two samples by $\sim 0.1\%$, in accordance with the overall agreement between the two experimental patterns. Surprisingly, this small difference is enough to account for the subtle differences in the two experimental patterns in the thickness ranges 12–14, 21–23, and 30–31 MLs, all in the vicinity of nodal points. Overall, the strain is small, less than 2% initially, and decays with the increasing film thickness to less than 1% beyond 10 MLs and diminishes around 30 MLs. The average strain in a 30 ML film is $\sim 0.9\%$, within the range of general estimation.¹⁷

Recently, Miller *et al.* have shown a fundamental phase relationship between the oscillations of surface energy and

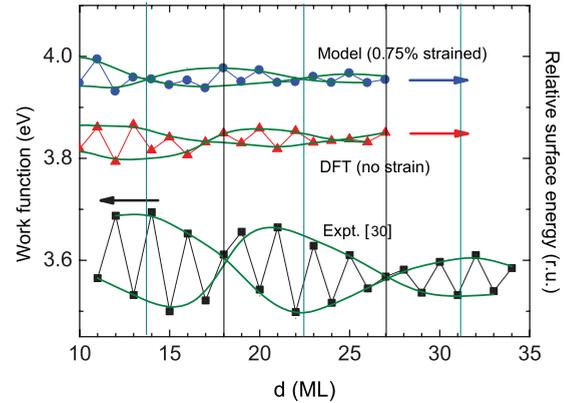


FIG. 6. (Color online) Comparison of an experimental work function pattern³⁰ with a DFT calculated surface energy pattern without strain and with a model predicted surface energy pattern with 0.75% strain. Note the 1/4 of a period of phase shift between the experimental data and model prediction.

of work function that their beating patterns are always offset by 1/4 of a period.²⁸ We have shown that the strain can not only change the odd-even oscillations but also shift the phase of beating patterns of surface energy.²⁹ Applying Miller’s phase relation to the Si-supported Pb(111) film by assuming that the interface shifts the work function and surface energy phase together, we can fit the phase of a surface energy beating pattern to match (by an offset of 1/4 of a period) the experimental phase of a work function pattern, such as the one measured by Qi *et al.*,³⁰ using strain as a fitting parameter. We obtained the best fit with an average 0.75% strain for this particular film, as shown in Fig. 6.

In conclusion, we have developed a theoretical framework to investigate the interplay between the QSE and strain effect on the thermodynamic stability of metal nanofilms, through the introduction of a new concept of quantum electronic stress.¹⁹ In the present case, the quantum electronic stress represents the additional quantum oscillations of surface stress induced by the QSE. Broadly, our theoretical framework can be extended to investigate the interplay between the QSE and strain effect on a range of kinetic and thermodynamic growth properties, such as surface adsorption and diffusion and step-edge barrier, where quantum “adsorption”³¹ and “diffusional” stress³² induced by the QSE can be derived from first-principles to play the role of quantum surface stress here. Thus, our theory will be applicable to both thermodynamic and kinetic properties of nanoscale thin films when the QSE and strain effect are prominent.

Note added. After submitting our paper, we become aware of another related work showing quantum oscillations of surface stress induced by the QSE in Al film on Si (Ref. 33).

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