Observation of Γ-point phonon frequency in ultrathin metallic films confirmed by *ab initio* calculation and lattice dynamics

H. Tanei, K. Kusakabe, H. Ogi,[a] N. Nakamura, and M. Hirao
Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

(Received 22 April 2009; accepted 29 May 2009; published online 6 July 2009)

Vibrations in ultrathin metallic films excited by ultrafast light pulses have been studied based on continuum mechanics. However, this paper shows that they are Γ-point phonon vibrations of plate-phonon modes. *Ab initio* and lattice dynamics calculations are made to compare Γ-point phonon vibrational frequencies with measurements obtained by the picosecond ultrasound spectroscopy. The standing-wave frequencies of specific Γ-point phonon modes of the slab model show good agreement with measurements without any fitting parameters. This study informs us of a limitation of the continuum-mechanics theory for explaining the mechanics of ultrathin metallic films. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3157138]

Elastic property of ultrathin metallic films has been intensively studied in this decade for two reasons. First, it is indispensable to design micro-electro-mechanical systems/nano-electro-mechanical systems (MEMS/NEMS). High frequency resonators, for example, require the elastic constants of their components because they govern the resonant frequency.[1,2] Second, elasticity of ultrathin metallic films is barely grasped. Ultrathin films involve nanodefects,[3] noncohesive grain bonds,[4] huge intrinsic residual strain,[5–7] and large surface energy;[8] all of them affect the elastic constants, but their contributions remain unclear.

For ultrathin films (~20 nm) composed of light elements, such as LiBr and MgO, high-resolution electron-energy loss spectroscopy (HREELS) was applied to study surface phonon behaviors, and previous studies show that the dispersion relationship or the thickness dependence of surface phonon frequency departs from the prediction by the dielectric approximation model when the film thickness is thinner than ~3 nm.[9–11] The deviation from the macroscopic prediction was attributed to the detection of longitudinal standing-wave resonances confined in the film, and the lattice dynamic model[12] explained the observed vibrational frequencies.

The HREELS method is thus powerful tool to study the elastic and optical properties of ultrathin films, but it would be inapplicable to metallic thin films composed of heavy elements such as Pt and Pd, which are important engineering materials for MEMS and NEMS applications, because of their much lower phonon vibrational frequencies and larger absorption loss. Many measurement methods have been then developed for elasticity of metallic thin films, including microtensile tests, microbending tests, nanoindentation, Brillouin scattering, surface acoustic waves, resonance ultrasound spectroscopy, and picosecond ultrasound, as reviewed in Ref. 13. Among them, picosecond ultrasound is the most promising method because it is a noncontacting method, being free from ambiguous influences by gripping, clamping, and sliding of the specimen. It is capable of evaluating elasticity of ultrathin metallic films as thin as 5 nm.[14,15] It is based on the pump-probe picosecond ultrasound technique using ultrafast light pulses. Thomsen *et al.*[16] succeeded in observing oscillations in the reflectivity change of the probe light pulse. They considered that this reflectivity oscillation was caused by the mechanical oscillation of the thin film and evaluated the sound velocity of thin films using the continuum mechanics. Following this discovery, Perrin *et al.*[17] detected the oscillation in Cu/W superlattice and discussed softening of the elastic constants. Ogi *et al.*[14] observed the reflectivity oscillations in ultrathin Pt films and showed their stiffening behavior. Nakamura *et al.*[18] observed recovery of elastic constant in ultrathin polycrystalline Cu films and revealed very stable elasticity in ultrathin epitaxial Cu films on silicon.[19]

These previous studies have taken the reflectivity oscillation as the mechanical resonant vibration and adopted the continuum mechanics theory. Indeed, the oscillation frequency was apparently proportional to the reciprocal of the film thickness, and the resonant frequency f was explained by the conventional relationship with the thickness D as $f=v/2D$ (v is the sound velocity), when the acoustic impedance of the substrate is smaller than that of the film. Such understanding allowed evaluation of the out-of-plane elastic constant C_{33} (when the x_3 axis is taken in thickness direction) of ultrathin films. However, it is doubtful whether the continuum mechanics explains the elastic properties of the films and the following question always arises: "At what point does classical continuum mechanics break down and atomistic mechanics begin to dominate?"

In this study, we measure the vibrations from ultrathin noble-metal films after the excitation by the pump light pulse using the ultrafast picosecond ultrasound technique and compare them with the one-dimensional lattice dynamics model and the *ab initio* calculation model. We develop slab models consisting of thick enough vacuum layers and 5–11 atomic layers in the unit cell, focusing the phonon frequencies with the in-plane-direction wave number.

Pt and Pd films (5–40 nm thick) are deposited on (001) Si substrates by magnetron sputtering technique. X-ray diffraction (XRD) method confirms that their [111] crystallographic orientation is almost completely aligned in the film thickness direction. We also deposit Pt on (001) MgO substrates to make Pt(001) epitaxially grow. The MgO-substrate temperature is kept at 500 °C after the deposition, and the specimens are cooled down to 200 °C at 4 °C/min, and then they are cooled slowly to room temperature in the chamber. This procedure can grow epitaxial Pt thin film in

[a]Electronic mail: ogi@me.es.osaka-u.ac.jp.

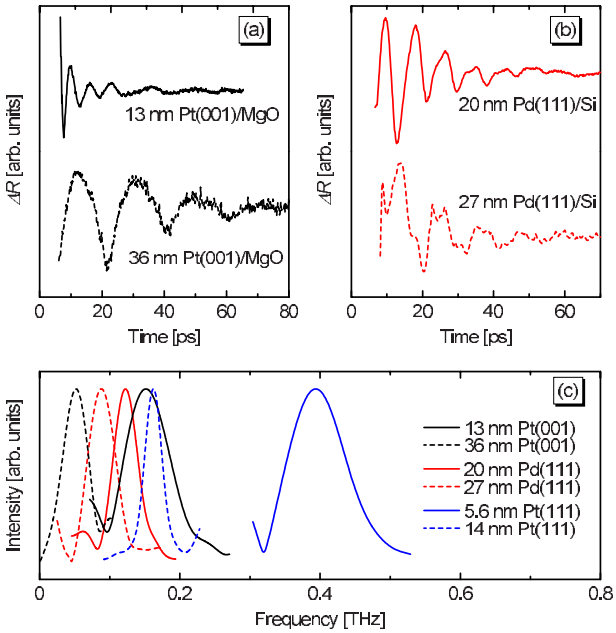

FIG. 1. (Color online) Time-resolved reflectivity changes for (a) 13 and 36 nm Pt(001) films on MgO substrate and (b) those for 20 and 27 nm Pd(111) films on Si substrates. (c) Their Fourier spectra including those from 5.6 and 14 nm Pt(111) films on Si substrates. The oscillation frequency appears to be inversely proportional to the film thickness.

[001] direction. The out-of-plane and in-plane XRD methods confirm that they are single crystal thin films. The thicknesses of the films are determined by the x-ray reflectivity method, where x rays reflected at the film surface and film-substrate interface interfere to cause oscillations in the reflectivity profile, which gives the film thickness by fitting the theoretical curve.[20]

The ultrafast picosecond-ultrasound spectroscopy[14] is applied to the ultrathin films. The details of the measurement setup are shown in Ref. 15. Figure 1 shows examples of the time-resolved reflectivity changes, causing vibrations. Their Fourier spectra indicate that the peak frequencies appear to be inversely proportional to the film thicknesses, suggesting that the vibration in the film can be considered as a mechanical resonance governed by the continuum mechanics. However, the thicknesses of the deposited thin films are less than 40 nm and the continuum mechanics could be physically inapplicable to such ultrathin films.

We consider that the incident probe light pulse excites the plate-wave mode whose wave number vector is parallel to the in-plane direction. Because the film thickness is extremely smaller than the laser spot diameter (~ 10 μm), the in-plane-direction wave number equals nearly zero and nonpropagating plate-wave modes are principally excited. Such a vibration corresponds to a phonon vibration at the Γ-point of the in-plane-propagating modes, not the acoustic mode. Therefore, we construct slab models and calculate the Γ-point phonon-mode frequency using *ab initio* calculation.

The slab models consist of 5–11 atomic layers and thick enough vacuum layers; The vacuum layers allow us to make the interlayer interaction ineffective. Their thickness is more than twice of the slab thickness. We construct Pt(111), Pt(001), and Pd(111) slab models; for example, Pt(111) represents that (111) planes of Pt are stacked so as to be parallel to the surface. Each plane in the slab contains one atom, and the structure is optimized fixing the transverse isotropic symmetry. The structure optimization is performed by PWSCF code,[21] which is based on a plane-wave pseudopotential approach to the density-functional theory.[22,23] The exchange correlation functional is treated using the local density approximation. The energy cutoff value of the plane-wave expansion for the wave function is 30 Ry and that of the charge density is 150 Ry. The k-point mesh for the calculations is $8\times8\times1$ Monkhorst–Pack scheme.[24] After the optimization, the atomic forces are less than 10^{-6} Ry/Å, the stresses were less than 3 MPa, and the energy variation from the iteration is less than 10^{-8} Ry, which indicates that the obtained structure are well optimized. Figure 2 compares the in-plane lattice distance a and the atomic layer distance d of the slabs after the structure optimization with those of the stress-free bulk materials obtained by the *ab initio* calculation. The slab structures shrink in the in-plane direction and elongate in the out-of-plane direction compared with the bulk structures.

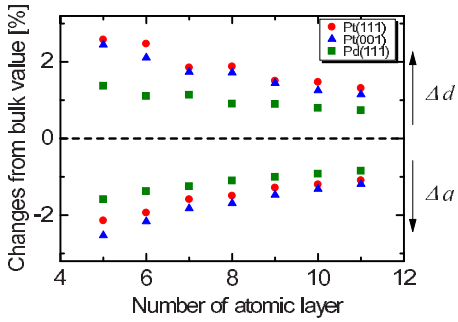

FIG. 2. (Color online) Differences of interatomic distances of the slab structures after optimization from corresponding stress-free bulk materials. a denotes the in-plane interatomic distance and d is the interlayer distance. Their bulk values are obtained by the *ab initio* calculation as a=2.7796, 2.7846, and 2.7444 Å, and d=2.2482, 1.9340, and 2.2394 Å for Pt(111), Pt(001), and Pd(111), respectively.

We then calculate the phonon frequency of the slab models using density functional perturbation theory.[25] Figure 3 shows example of calculated phonon-dispersion curves in the in-plane direction. (There is no mode softening, confirming the stability of the structure.) We focus the specific modes at the Γ-point, which have symmetric atomic displacements about the center plane (longitudinal standing resonances of the slab).

Figure 4 (solid marks) shows the Γ-point phonon frequencies versus the number of atomic layers. Higher vibrational frequencies of Pt(001) and Pd(111) slabs than those of Pt(111) slabs are caused by their smaller interlayer distances, and they do not reflect the stiffness difference. [Note that the longitudinal-wave modulus of Pt(111) is larger than those of Pt(001) and Pd(111).] We plot the measured vibration fre-

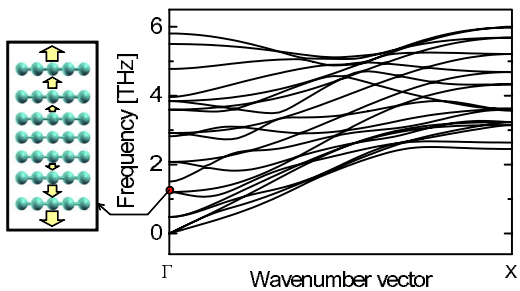

FIG. 3. (Color online) Phonon-dispersion curves of 7-layer Pt(001) slab along [100] direction. Marked Γ-point frequency is the longitudinal standing vibration, whose displacements are symmetric about the center of slab.

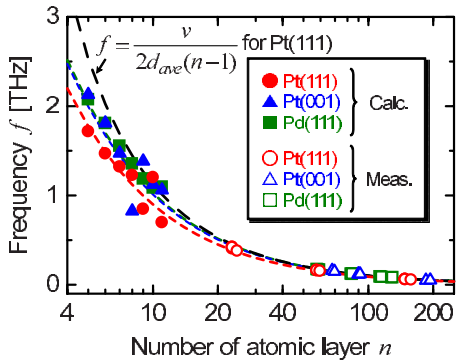

FIG. 4. (Color online) Measured and calculated phonon frequencies for ultrathin films and slab model. The colored broken lines represent the natural frequencies obtained by the one-dimensional lattice dynamics model (mass-spring model), whose spring constants are determined by the measurement of the thickest specimens. The black broken line is the resonant frequency of Pt(111) based on the continuum mechanics theory given by $f=v/2d_{\mathrm{av}}(n-1)$, where v and d_{av} represent sound velocity and average interplane distance, respectively.

quencies of the reflectivity of the probe light pulse in Fig. 4 by open marks.

In order to compare the measurement with the *ab initio* calculation, we calculate the natural frequencies of the mass-spring model as a typical discrete system (one-dimensional lattice dynamics model). It simply consists of the equal-mass points connected by springs with spring constant k. Assuming harmonic vibrations, equations of motion for all the mass points lead to an eigenvalue problem, and the longitudinal standing-wave resonance frequency is obtained from the smallest eigenvalue of the system. We determine the spring constant k so as to provide the measured frequency of the thickest specimens. The *ab initio* calculation does not include any experimental parameters, and then the calculated and measured frequencies are completely independent. Nevertheless, the measured and calculated frequencies show good agreement with the natural frequencies, clearly indicating that the observed vibration of the reflectivity in the ultrathin film is the Γ-point phonon frequency of the plate mode, neither a resonant mode in the continuum mechanics nor the acoustic-mode phonon vibration.

To investigate the limitation of the continuum mechanics, we calculate the resonant frequency of the Pt(111) film by $f=v/2D=v/2d_{\mathrm{ave}}(n-1)$, assuming the continuum mechanics. The result is shown in Fig. 4 by the black broken line, where d_{ave} is the average interplane distance of calculated bulk Pt(111). Comparing the red marks (*ab initio* calculation) and the black broken line (continuum mechanics model), the difference in their frequencies becomes significant, when the number of atomic layer is smaller than 20. The continuum mechanics thus fails to apply to ultrathin films. The atomic radius and charge distribution at the surface have great influence on the film thickness, making the definition of thickness difficult. Thus, the analysis for the reflectivity vibration by continuum mechanics is physically incorrect, although the discrepancy becomes insignificant when the number of atomic layers is larger than 50.

Our slab model is a film-shaped perfect crystal, and does not consider the film-substrate interface and the surface rearrangement. However, the frequency of the fundamental longitudinal resonance mode is less sensitive to the surface and interface, because the stress becomes negligible there. It is important in the theoretical point of view that the *ab initio* calculation is well applicable to the prediction of phonon vibrations in ultrathin metallic films, even when rearrangements at surface and interface are discounted.

In summary, the essential nature of oscillations in reflectivity change observed by ultrafast picosecond-ultrasound spectroscopy is clarified by *ab initio* and lattice dynamics calculations. The Γ-point frequencies of the in-plane plate modes are focused and calculated using the slab models. The measured frequencies and the Γ-point phonon frequencies show good agreement with those calculated by the lattice dynamics model despite that the *ab initio* calculation does not involve any fitting parameters. This result strongly indicates that vibrations of ultrathin films are the Γ-point phonons, neither the acoustic (propagating) modes nor the resonance modes in the continuum mechanics. The continuum mechanics is estimated to break down for ultrathin films with less than 20 atomic layers. The experiments made here are for thin films thicker than in the theoretical approach and our future work will involve experiments for thinner films, by improvements of specimens and optics, and computations for thicker films to overlap them in the same thickness range.

[1] N. Fang, D. Xi, J. Xu, M. Ambati, W. Srituravanich, C. Sun, and X. Zhang, Nature Mater. **5**, 452 (2006).
[2] J. H. Bak, Y. D. Kim, S. S. Hong, B. Y. Lee, S. R. Lee, J. H. Jang, M. Kim, K. Char, S. Hong, and Y. D. Park, Nature Mater. **7**, 459 (2008).
[3] H. Ogi, G. Shimoike, M. Hirao, K. Takashima, and Y. Higo, J. Appl. Phys. **91**, 4857 (2002).
[4] N. Nakamura, H. Ogi, and M. Hirao, Acta Mater. **52**, 765 (2004).
[5] J. A. Floro, S. J. Hearne, J. A. Hunter, P. Kotula, E. Chason, S. C. Seel, and C. V. Thompson, J. Appl. Phys. **89**, 4886 (2001).
[6] M. Chhowalla and H. E. Unalan, Nature Mater. **4**, 317 (2005).
[7] M. M. Roberts, L. J. Klein, D. E. Savage, K. A. Slinker, M. Friesen, G. Celler, M. A. Eriksson, and M. G. Lagally, Nature Mater. **5**, 388 (2006).
[8] J. J. Métois, A. Saúl, and P. Müller, Nature Mater. **4**, 238 (2005).
[9] W. Gao, Y. Fujikawa, K. Saiki, and A. Koma, Solid State Commun. **87**, 1013 (1993).
[10] P. Senet, Ph. Lambin, and A. A. Lucas, Phys. Rev. Lett. **74**, 570 (1995).
[11] L. Savio, E. Celasco, L. Vattuone, M. Rocca, and P. Sent, Phys. Rev. B **67**, 075420 (2003).
[12] Ph. Lambin, P. Sent, and A. A. Lucas, Phys. Rev. B **44**, 6416 (1991).
[13] H. Ogi, N. Nakamura, H. Tanei, and M. Hirao, *Proceedings of the Materials Research Symposium Vol. 875*, edited by T. E. Bucheit, A. Minor, R. Spolenak, and K. Takashima (MRS, Warrendale, Pennsylvania, 2005), pp. o1.1.1–12.
[14] H. Ogi, M. Fujii, N. Nakamura, T. Yasui, and M. Hirao, Phys. Rev. Lett. **98**, 195503 (2007).
[15] H. Ogi, M. Fujii, N. Nakamura, T. Shagawa, and M. Hirao, Appl. Phys. Lett. **90**, 191906 (2007).
[16] C. Thomsen, J. Strait, Z. Vardeny, H. J. Maris, J. Tauc, and J. J. Hauser, Phys. Rev. Lett. **53**, 989 (1984).
[17] B. Perrin, B. Bonello, J.-C. Jeannet, and E. Romatet, Physica B **219–220**, 681 (1996).
[18] N. Nakamura, H. Ogi, T. Shagawa, and M. Hirao, Appl. Phys. Lett. **92**, 141901 (2008).
[19] N. Nakamura, H. Ogi, and M. Hirao, Phys. Rev. B **77**, 245416 (2008).
[20] L. Parratt, Phys. Rev. **95**, 359 (1954).
[21] S. Baroni, A. D. Corso, S. Gironcoli, and P. Giannozzi, http://www.pwscf.org/.
[22] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[23] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[24] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[25] S. Baroni, S. Gironcoli, A. D. Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).