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Unusual Temperature Dependence of Elastic Constants of Pt and Pd Studied by Picosecond Ultrasounds and Ab initio Calculation

ピコ秒超音波と第一原理計算を用いたPtおよびPdの弾性定数の異常温度依存性の研究

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1. Introduction

The elastic constants of solids generally increase as temperature decreases because of anharmonicity of interatomic potentials. For example, those of Cu[1], showing three independnet elastic constants C_{11}, C_{12} and C_{44}, increase with cooling down from room temperature, and they remain uncahnged below about 100 K since the invariability of interatmic distances caused by the effect of zero-point energy [**Fig. 1(a)**]. Varshni[1] approximated the tenperature dependence of an elastic constant C_{ij} by the following formula

$$C_{ij}(T) = C_{ij}^0 - \frac{s}{e^{t/T} - 1}. \quad (1)$$

Here, T, C_{ij}^0, s and t denote temperature, the elastic constant at 0 K, and parameters, respectively. However, as seen in **Figs. 1(b) and (c)**, temperature dependences of elastic constants of Pd[2] and Pt[3] show unusual behavior in spite of their normal thermal expansion at low temperatures[4-6]. In the case of Pt, only two values, C_{44} and $C'=(C_{11} - C_{12})/2$ were reported. Therefore, we could not determine the temperature dependence of all elastic constants and show only C_{44} in Fig. 1(c).

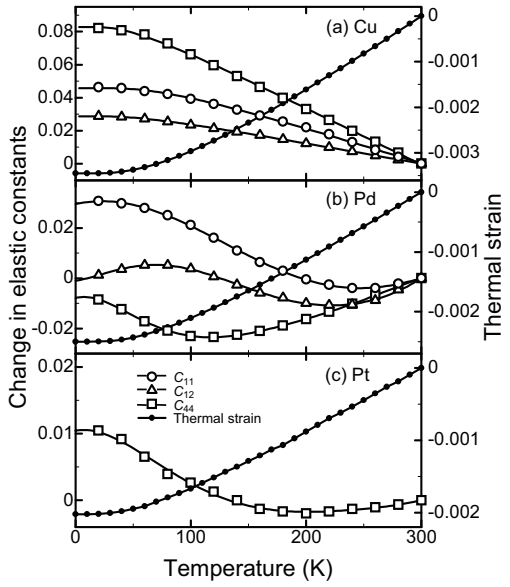

Fig. 1 Temperature dependences of elastic constants[1-3] (open dots) and thermal strain[4-6] (close dots) of Cu, Pd and Pt.

Pd, Pt and their chemical compounds are important material used for catalysts, which are intensively researched. However, the origin of such unusual elasticity remains unclear. In this study, we prepare Pd and Pt thin films and measure their temperature dependence of elastic stiffness using picosecond laser ultrasounds (PSLU) because it is noted that the effect of surface energy or existence of huge strain may make the elastic properties of thin films different from those of bulk materials[7]. With the aim of discussing about solid-state physics, for example interatomic potentials and surface energy, we also perform theoretical analyses using *ab initio* calculation based on density functional theory (DFT)[8,9].

2. Measurements

Thomsen and co-workers first detected high frequency coherent acoustic phonons using ultrafast pump-probe light pulses[10]. Following their work, the picosecond ultrasound techniques were developed for the study of ultrahigh frequency acoustic properties of solids. The pump-probe method determines the out-of-plane elastic stiffness from the velocity of the longitudinal wave propagating along the thickness direction. Both generation and detection are carried out by femtosecond light pulses. When the film thickness is smaller than the wavelength (~30 nm, depend on the material), we observe phenomenon called the acoustic phonon resonance[7], where the standing waves in a thin film are measured to evaluate the elasticity through their resonance frequencies.

Fig. 2 shows optics we developed for this study. We irradiate a second-harmonic-generator (SHG) crystal with a titanium-sapphire pulse laser at 800 nm wavelength and 100 fs pulse width. SHG generates the frequency-doubled pulse, and then they are separated into the pump light (λ = 800 nm) and the probe light (λ = 400 nm) by a dichroic mirror. The former is focused on the specimen to

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generate an acoustic pulse through instantaneous thermal expansion. The latter is used to detect generated acoustic pulse. The probe light is delayed by moving of the corner reflector, and the signals are detected as changes in the amplitude and phase of the reflected light. The specimen is held in the cryostat and cooled through the Cu heat exchanger down to liquid helium temperature.

We deposit Pd and Pt thin films by RF magnetron sputtering on (001) face of monocrystal Si substrates. Their thicknesses are 29.5 and 29.6 nm, which are determined by the x-ray total reflectivity measurement. The high-angle x-ray diffraction (XRD) measurement is also performed to evaluate the crystallographic orientation, which confirms strong (111) texture for both thin films.

3. Ab initio Calculation

We perform *ab initio* calculations using the PWscf code[11], which is based on a plane-wave (PW) pseudopotential approach to DFT. The exchange correlation function is treated using the generalized gradient approximation. We use a face-centered cubic unit cell containing 4 atoms. A $10\times10\times10$ Monkhorst-Pack grid is used for *k*-point sampling of the Brillouin zone. The energy cutoff value of the plane-wave expansion for wave functions is 1.36×10^3 eV, and that of the charge density is 1.36×10^4 eV. These conditions give fluctuations in the lattice parameters smaller than 0.5 %. We then calculate the elastic constants of these structures using the harmonic-lattice approximation. The total energy is calculated by changing various strains from -0.01 to 0.01 by a 0.002 step, and a quadratic function is fitted to the energy-strain plot. To simulate the effect of thermal expansions, we change the lattice parameters in accordance with reported thermal expansion coefficients[4-6]. Thus, we estimate the elastic constants affected by thermal phonons through the volume change.

4. Results and Discussion

Figs. 3(a) and (b) show the temperature dependence of elastic constant $C^{<111>}$ of the Pd thin film obtained by PSLU measurements and that of bulk Pd single crystal computed from reported C_{ij}[2], respectively. As seen in Fig. 3(b), the temperature dependence of $C^{<111>}$ of bulk Pd shows unusual behavior, showing a local minimum value at 200 K. The Pd thin film, on the other hand, shows larger changes in the modulus, which is clearly different from bulk Pd. **Fig. 3(c)** shows effect of thermal expansions on the $C^{<111>}$ of single crystal Pd estimated by *ab initio* calculations. The results show normal temperature dependence, indicating that thermal phonon is not the dominant factor of the unusual temperature dependence of Pd.

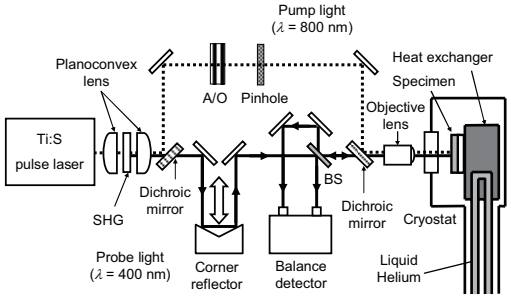

Fig. 2 Schematic of developed optical system for low-temperature pump-probe measurement.

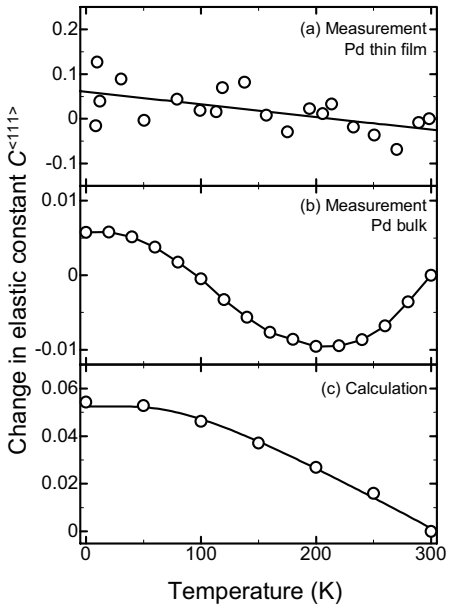

Fig. 3 Temperature dependences of elastic constant $C^{<111>}$ of Pd thin films obtained by PSLU measurements (a), bulk Pd single crystal[2] (b). And the effect of thermal expansions on the modulus of single crystal Pd estimated by *ab initio* calculations(c).

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