Picosecond ultrasound at low temperatures for Pd thin films*

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Abstract
In this study, we develop the picosecond ultrasound method to observe ultrasonic pulse-echo signals in palladium thin films with the thickness of less than 100 nm. Specimens are cooled with liquid helium through a heat exchanger in a cryostat, and an ultrahigh-frequency acoustic pulse is generated by a femtosecond light pulse, which propagates in the film-thickness direction. Pulse echoes of the acoustic pulse are observed as changes in reflectivity of time-delayed probe light. Because the pulse-echo measurement can provide the longitudinal-wave out-of-plane elastic constant of films, it will be useful for the study of temperature dependence of the elastic constant of thin films.

Key words: Palladium, Thin Films, Picosecond Ultrasounds, Elastic Constants, Low Temperatures

1. Introduction
The elastic constants of solids generally increase as temperature decreases because of anharmonicity of interatomic potentials. For example, those of Cu\(^{10)}\), showing three independent elastic constants \(C_{11}, C_{12}, \) and \(C_{44}\), increase with cooling down, and they are almost constant below 100 K since the invariability of interatomic distances\(^{2)}\) caused by the effect of zero-point energy. Varshni proposed following formula as a general temperature dependence of elastic constants\(^{1)}\),

\[
C_\alpha(T) = C_\alpha^0 - \frac{s}{e^{t/T} - 1},
\]

Here, \(T\), \(C_\alpha^0\), \(s\), and \(t\) denote temperature, the elastic constant at 0 K, and parameters, respectively. However, temperature dependences of elastic constants of Pd\(^{3)}\), especially \(C_{44}\) show unusual behavior in spite of their normal thermal expansion at low temperatures\(^{4)}\). It does not show monotonic increase as the decrease of temperature. A contribution of electronic band structure is suggested as a possible cause\(^{5)}\), but its detail remains unclear. In order to understand the physical reason for Pd’s unusual elasticity, we aim to reveal the relationship between the contributions of electron and phonon (band structure and lattice vibration).

In this study, we develop a picosecond ultrasound method\(^{6)}\) to observe ultrasonic pulse-echoes in Pd thin films at cryogenic temperatures. The reason of the low temperature measurement is that very large changes in interatomic distances can be achieved in thin films because of the less mobility of dislocations. In addition, considering the thermal expansion coefficient mismatch between films and substrates, strong in-plane tensile strain occurs in the films with cooling. Therefore, out-of-plane interatomic distances in the films should decrease enormously at low temperatures, which are never achieved for bulk...
In such a strained structure, the lattice anharmonicity becomes significant and the lattice vibration contribution will be enhanced, leading to the estimation of the contribution of the lattice anharmonicity effect to the temperature dependence of the elastic constants. Because the elastic constant can be obtained from the pulse-echo round trip time, observing the pulse-echo signals for thin film at low temperatures will contribute to evaluate the temperature dependence of the elastic constant.

2. Experimental

We deposit Pd thin films by RF magnetron sputtering on a (100) surface of monocrystal Si substrates. Before the deposition, the surface of the substrate is cleaned by piranha solution (98% H$_2$SO$_4$ : 33% H$_2$O$_2$ = 7:3) and rinsed with ultrapure water. The film thickness is 95.1 nm, which is 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 (Fig. 1).

Thomsen and coworkers first generated and detected a high-frequency coherent phonon pulse in a thin film using ultrafast pump-probe light pulses. This method has been used to study ultrahigh-frequency acoustic properties of solids, which is efficient for accurate evaluation of the elastic constants of thin films. We develop an optical system with a cryostat for picosecond ultrasound measurements at low temperatures (Fig. 2). The specimen is set in the cryostat and cooled by liquid He through a Cu heat exchanger. The pressure inside the cryostat is maintained below 1.0×10$^{-3}$ Pa by a turbo molecular pump (TMP), achieving effective thermal insulation. We can conduct the picosecond ultrasound
measurements through a quartz window of the cryostat. A titanium-sapphire pulse laser with 800-nm wavelength and 140-fs pulse duration is separated into the pump light and the probe light by a half-wavelength plate ($\lambda/2$) and a polarization beam splitter (PBS). The former is delayed by moving a corner reflector and modulated by an acoustooptic modulator (A/O) with a modulation frequency of 100 kHz. Then its first-order diffraction light is selected by a pin-hole and focused on the specimen to generate an ultrahigh-frequency (~50 GHz) acoustic pulse through an instantaneous thermal expansion, traveling along the film thickness direction. The acoustic pulse is reflected from the interface between films and substrates. Meanwhile, a second-harmonic-generator (SHG) crystal is irradiated with the latter, which generates frequency-doubled light. Generated light pulse at 400-nm wavelength is perpendicularly focused on the surface of the specimen to detect acoustic pulse echoes, which are obtained by changes in reflectivity. They are detected by a balanced detector, and their 100 kHz components are extracted by a lock-in amplifier. Round-trip times of the ultrasonic pulse echoes are measured, which will be used to determine the longitudinal sound velocity along the film thickness direction.

The out-of-plane elastic stiffness $C_\perp$ of the film is given by

$$C_\perp = \rho (2d/\Delta t),$$

where $\rho$, $d$, and $\Delta t$ are mass density, film thickness, and the round-trip time, respectively. The film thickness $d$ is determined accurately by the XRR measurement. We use the mass density $\rho$ of bulk materials to calculate the elastic stiffness of thin films. Two causes, volume defects and changes in the interatomic distance, may affect the mass density of thin films. However, the XRD measurement shows that the fractional change in the interatomic distance is on the order of $10^{-3}$, and its effect on the mass density is negligible. The other cause, volume defects, is also negligible because they are expected to be zero-volume defects, for example, incohesive bonds between grains.

![Fig. 3 Multiple reflection echoes of a longitudinal acoustic pulse within a Pd thin film deposited on a (001) Si substrate observed at room temperature and 20 K; (a) Signals as measured; (b) Extracted pulse echoes by removing thermal backgrounds.](image-url)
3. Results and discussion

Using developed optics, we conduct the pump-probe picosecond ultrasound measurements for Pd thin films deposited on Si substrates. Figure 3(a) shows as-measured changes in intensity of reflected probe light at room temperature and 20 K. The rising edges indicate the incident times of the pump-light pulse, after that the reflectivity decays exponentially because of diffusion of thermal phonons excited by the pump light pulse. We can find some dips in the reflectivity with a constant time interval, which is considered as the reflection echoes of the longitudinal acoustic pulse within the film. We assume the thermal effects as backgrounds and remove their responses by approximating them by low-order polynomial functions using the least-square method. Figure 3(b) shows the background subtracted reflectivity changes, where we clearly observe the pulse echoes of the longitudinal wave, from which the round-trip times can be determined. It means that we succeed the low-temperature ultrasound measurements for Pd thin films. This achievement will allow us to evaluate the temperature dependence of elastic stiffness of Pd thin films; it will be our future work.

4. Conclusion

In this study, a pump-probe method for low-temperature picosecond ultrasound measurements is developed. We generated and detected ultrahigh-frequency acoustic phonon pulses in Pd thin films deposited on monocrystal Si substrates at room temperature and 20 K. Multiple reflection echoes for Pd thin films are observed at cryogenic temperature. The result will allow us to evaluate the temperature dependence of elastic stiffness of Pd thin films.

References