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Ultrasonic Study of Vacancy in Single Crystal Silicon at Low Temperatures

M Akatsu[1], T Goto[1], H Y-Kaneta[2], H Watanabe[1], Y Nemoto[1], K Mitsumoto[1], S Baba[1], Y Nagai[1] and S Nakamura[3]

[1] Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan
[2] Center of Quantum Materials Science, Niigata University, Niigata 950-2181, Japan
[3] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

E-mail: akatsu@phys.sc.niigata-u.ac.jp

Abstract. We have performed ultrasonic measurements at low temperatures in order to investigate vacancy in single crystal silicon. The longitudinal elastic constants of non-doped and boron-doped silicon grown by a floating zone method exhibit appreciable softening with decreasing temperature down to 20 mK. The softening of boron-doped silicon is easily suppressed in applied magnetic field up to 2 T, while the softening of non-doped silicon is robust in fields even up to 16 T. The softening of elastic constants in high-purity crystalline silicon is certainly caused by the coupling of elastic strains of the ultrasonic waves to electric quadrupoles of the vacancy orbital.

1. Introduction

Single crystal of silicon grown by a floating zone (FZ) method is one of the most pure and ideal crystals. From the entropy term of the free energy of silicon crystal grown at 1412°C, however, native point defects exist essentially in single crystal silicon. The point defects are vacancy created by a missing atom and interstitial defined as an atom occupying an interstitial site. To yield either the vacancy or the interstitial is dominated by the rate of the crystal growth [1]. The wafer of vacancy-rich silicon crystal is generally adopted in electronic device. The vacancies aggregate to form voids with about 20-300 nm in size, which gives rise to serious damage in device fabrications. Therefore, silicon industries use perfect silicon crystal in addition to annealed wafers and epitaxial wafers. The perfect silicon crystal means a void-free silicon crystal within isolated vacancies. The isolated vacancies play an important role for dopant diffusion, oxygen precipitate in silicon wafer. Consequently, the direct observation of vacancy and estimation of vacancy concentration in silicon crystal are one of the most important issues in semiconductor physics and electronic device technology. The electron paramagnetic resonance (EPR) and positron annihilation γ-ray measurements are performed for the observation of vacancy and its concentration in silicon crystal, in which the vacancy concentration was artificially enhanced [2, 3]. The vacancy in silicon crystal has various charge states distinguished by the number of electrons existing in the vacancy. Because the charge states V^+ of vacancy with three electrons in boron-doped silicon and V^- of vacancy with five electrons in phosphor-doped silicon have magnetism, there vacancies can be observed by ESR measurements. The vacancy with four electrons in non-doped silicon, which possesses non-magnetic character, is unable to observe by EPR measurements. The observation of isolated vacancy of silicon crystals of commercial-based vacancy concentration has not been reported so far. We have recently succeeded in the observation of the isolated vacancy in single crystal silicon by using ultrasonic measurements at low temperatures [4]. In the present paper we show the results of ultrasonic investigations on the vacancy of single crystal silicon.

2. Experiment

We measured the ultrasonic velocity v of two kinds of samples of silicon, which are non-doped and boron-doped single crystals of silicon grown by a floating zone (FZ) method. The ultrasonic velocity was measured by an ultrasonic pulse-echo method. The elastic constants C of samples were estimated by $C = \rho v^2$ with the mass density $\rho = 2.33$ g/cm^3. In the present experiments the ultrasonic wave was generated and detected by the piezoelectric ZnO sputtered film on a surface of sample, because the bond between the sample and piezoelectric $LiNbO_3$ plates used in the conventional ultrasonic measurements breaks from a negative thermal expansion coefficient of silicon at low temperatures [5]. We employed ZnO film with thickness 10 μm for the longitudinal ultrasonic wave with frequency of 400 MHz. For the low-temperature ultrasonic measurements, we used a ^{3}He-^{4}He dilution refrigerator (Oxford Instruments) down to 20 mK and a homemade ^{3}He refrigerator above 400 mK.

3. Results and discussion

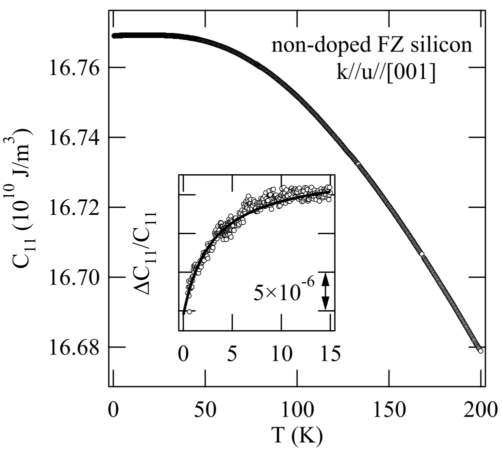

Figure 1. Temperature dependence of the elastic constant C_{11} of non-doped FZ silicon. The inset shows the low-temperature behavior of C_{11}. The solid line is a fit to Eq. (1) described in the text.

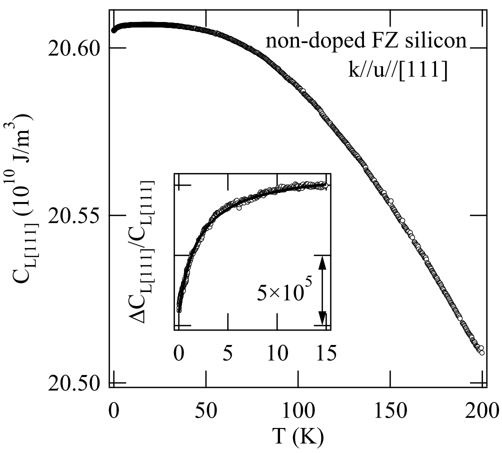

Figure 2. Temperature dependence of the elastic constant $C_{\mathrm{L}[111]}$ of non-doped FZ silicon. The inset shows the low-temperature behavior of $C_{\mathrm{L}[111]}$. The solid line is a fit to Eq. (1) described in the text.

In Fig. 1 we show the temperature dependence of the elastic constant C_{11} of non-doped FZ silicon. The $C_{11} = C_{\mathrm{B}} + (4/3)(C_{11} - C_{12})/2$ was measured by the longitudinal ultrasonic wave propagating along the [001] axis, which induces the elastic strain $\epsilon_{zz} = (1/3)\epsilon_{\mathrm{B}} + (1/\sqrt{3})\epsilon_u$. Here, the volume strain ϵ_{B} with Γ_1 symmetry and the tetragonal strain ϵ_u with Γ_3 symmetry are responsible for the elastic constant $(C_{11} - C_{12})/2 = C_{\Gamma_3}$ and the bulk modulus C_{B}, respectively. The inset in Fig. 1 shows $\Delta C_{11}/C_{11}$ as a function of temperatures below 15 K. The C_{11} exhibits a softening of 1.4×10^{-5} below 15 K dawn to 0.5 K, while the C_{11} increases monotonously with decreasing temperature from room temperature.

Figure 2 and the inset reveals the temperature dependence of the elastic constant $C_{L[111]}$ of non-doped FZ silicon below 200 K and 15 K, respectively. We measured the $C_{L[111]} = C_B + (4/3)C_{44}$ by the longitudinal ultrasonic wave along the [111] axis, which induces $\epsilon_{L[111]} = (1/3)\epsilon_B + (2/3)(\epsilon_{yz} + \epsilon_{zx} + \epsilon_{xy})$. The trigonal strain $\epsilon_{yz} + \epsilon_{zx} + \epsilon_{xy}$ with Γ_5 symmetry is responsible for $C_{44} = C_{\Gamma_5}$. A monotonic hardening below 200 K and a softening of $\Delta C_{L[111]}/C_{L[111]} = 9 \times 10^{-5}$ below 15 K down to 25 mK with decreasing temperature are similar to the results of C_{11} in Fig. 1.

It is very interesting that C_{11} and $C_{L[111]}$ of the non-doped FZ silicon exhibit the elastic softening at low temperatures in Figs.1 and 2, because elastic constants show generally a hardening with decreasing temperature. Owing to using the high purity crystal of non-doped silicon, the low-temperature softening is attributed to intrinsic point defects of either vacancy or interstitial silicon. The non-doped FZ silicon crystal annealed for 10 hour at 1350 °Cin argon ambient shows a similar behavior to the softening of C_{11} in Fig. 1 [4]. This result strongly suggests that the elastic softening at low temperatures is caused by the vacancy.

In many cases the elastic softening with decreasing temperature is caused by the electronic states with orbital degrees of freedom of $4f$ electron in rare earth compounds and $3d$ electron in transition metal compounds. The vacancy state in silicon crystal has an A_1 singlet and a T_2 triplet split by cubic T_d site symmetry [6, 7]. In the charge state V^0 of vacancy with four electrons in non-doped FZ silicon, two electrons occupy the A_1 singlet with their spins paired. The other electrons go into the T_2 triplet with spin state $S = 0$, which possesses orbital degrees of freedom. Therefore, the vacancy state has five electric quadrupoles: O_u, O_v with Γ_3 symmetry and O_{yz}, O_{zx}, O_{xy} with Γ_5 symmetry. Because of the coupling of the quadrupole and the elastic strain with same symmetry, the elastic constants C_{11} and $C_{L[111]}$ of non-doped FZ silicon reveal the low-temperature softening described as

$$C_\Gamma = C_\Gamma^0 \frac{T - \Theta_\Gamma - \Delta_\Gamma^{JT}}{T - \Theta_\Gamma} \tag{1}$$

deduced from the quadrupole susceptibility [4]. Here, C_Γ^0 is a background of the elastic constant without quadrupole degrees of freedom. Θ means the energy of intersite quadrupole interaction, and Δ_Γ^{JT} is the Jahn-Teller energy. The analyses of the elastic softening of C_{11} and $C_{L[111]}$ in non-doped FZ silicon using Eq. (1) are shown in insets of Fig. 1 and Fig. 2, respectively. We assumed that the bulk modulus $C_B = 9.886 \times 10^{10}$ J/m^3 is independent on temperature below 15 K in the analyses. By fitting of the low-temperature softening of C_{11} in Fig. 1, $\Theta_{\Gamma_3} = -3$ K, $\Delta_{\Gamma_3}^{JT} = 0.14$ mK, $C_{\Gamma_3}^0 = 5.16246 \times 10^{10}$ J/m^3 are obtained. By fitting of the low-temperature softening of $C_{L[111]}$ in Fig. 2, $\Theta_{\Gamma_5} = -2$ K, $\Delta_{\Gamma_5}^{JT} = 0.4$ mK, $C_{\Gamma_5}^0 = 8.04093 \times 10^{10}$ J/m^3 are obtained. The negative Θ_Γ means the antiferro-type quadrupole interaction between the vacancies in the non-doped FZ silicon. From the Jahn-Teller energy Δ_Γ^{JT} written as $\Delta_\Gamma^{JT} = 2Ng_\Gamma^2/3C_\Gamma^0$, the vacancy concentration N can be estimated. Here, g_Γ is the coupling constant of quadrupole-strain interaction. The vacancy concentration in the non-doped FZ silicon is approximately estimated to $N \sim 10^{15}$ cm^{-3}.

To examine the magnetic field effects on the elastic softening, we measured the magnetic field dependence of $C_{L[111]}$ of non-doped FZ silicon in applied fields along the [111] axis, which shown in Fig. 3. The elastic softening of $C_{L[111]}$ in fields of 5 T and 10 T conform to the result in 0 T. This magnetic independent softening of $C_{L[111]}$ indicates the non-magnetic charge state V^0 resided four electrons at vacancy.

Figure 4 shows the temperature dependence of C_{11} of boron-doped FZ silicon under magnetic fields along the [001] axis. In zero field the C_{11} of boron-doped FZ silicon shows sharp softening below 2 K, while C_{11} of non-doped FZ silicon softens below 10 K. The softening of C_{11} of boron-doped FZ silicon reduces rapidly with increasing field up to 2 T, and is not shown in 5 T and

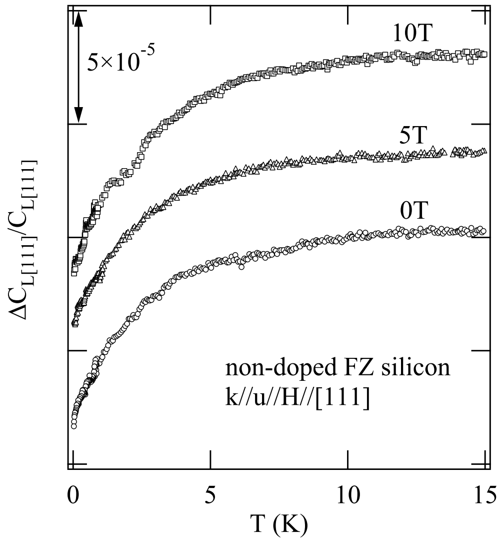

Figure 3. Temperature dependence of the elastic constant $C_{L[111]}$ of non-doped FZ silicon in applied magnetic field along the [111] direction.

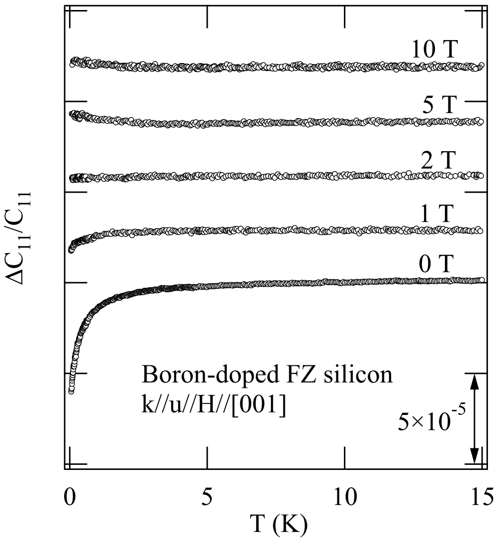

Figure 4. Temperature dependence of the elastic constant C_{11} of boron-doped FZ silicon in applied magnetic field along the [001] direction.

10 T.This behavior of boron-doped FZ silicon contrasts with the elastic softening of non-doped FZ silicon in fields, which is field independent. We conclude that the magnetic charge state V^+ of the vacancy in the boron-doped silicon causes the softening of C_{11} and its field dependence.

4. Conclusion

We have successfully observed the elastic softening of C_{11} and $C_{L[111]}$ in the non-doped FZ silicon and C_{11} in the boron-doped FZ silicon at low temperatures, which are caused by the isolated vacancy with cubic T_d-symmetry. The different behavior of elastic constant in magnetic fields suggests the non-magnetic charge state V^0 in the non-doped FZ silicon and the magnetic charge state V^+ in the boron-doped FZ silicon. Further ultrasonic measurements to elucidate vacancy in commercial-based CZ silicon crystal doped boron or phosphor are now in progress by our group.

Acknowledgments

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