

Surface acoustic wave diagnosis of vacancy orbital with electric quadrupoles in silicon

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Abstract. We demonstrate ultrasonic diagnosis of vacancies in boron-doped silicon wafers currently used in device manufacturing. The low-temperature softening of elastic constants measured by surface acoustic waves (SAW) as well as bulk ultrasonic waves is caused by a coupling of elastic strains to electric quadrupoles of the vacancy orbital in silicon wafers. Using interdigital transducers with a comb gap of 2.5 μm on a piezoelectric ZnO film deposited on the (001) surface of the wafer, we observed the softening of 1.9×10^{-4} in relative amount of the elastic constant C_s below 2 K down to 23 mK. Taking account of the strong quadrupole-strain interaction, we deduced a small vacancy concentration $3.1 \times 10^{12} \text{ cm}^{-3}$ in the surface layer of the wafer within a penetration depth 3.5 μm of the SAW.

1. Introduction

Silicon wafers are widely used for fabrication of semiconductor CMOS-devices of NAND flash memories, DRAM memories, and logic processors. The silicon wafers produced from Czochralski (CZ) silicon ingots contain intrinsic point defects of vacancy and silicon-interstitial. The growing rate in CZ silicon ingot affects character of the defect, namely fast rate favors vacancies and relatively slow rate brings silicon-interstitials. [1] The excess of the vacancies in the crystal growth forms voids, which have empty octahedral shape with 100 nm in typical size. The voids are recognized as crystal originated particles (COP), which are detected by laser light scattering measurements. [2, 3]

The micro-device fabrication pursuing large capacity and high-speed operation now adopts gate size beyond 19 nm. In order to realize optimum electrical properties and reduction of device failure,



precise controlling of bulk micro-defects as well as the voids is strongly required. It is supposed that the vacancies participate in creation of the bulk micro-defects in thermal processes in the device fabrication. The evaluation of the vacancy in silicon wafers will become crucially important for highly density semiconductors fabrication in industry. Because the semiconductor devices are fabricated using the active surface region within a few micrometer layer of silicon wafers, the vacancy evaluation of the surface layer of silicon wafer is particularly required.

Elastic strains associated with ultrasonic waves couple to electric quadrupoles of various quantum states with orbital degrees of freedom. We refer the quadrupole effects in 4f-orbital of rare-earth compounds [4], 3d-orbital in transition-metal compounds [5] and orbital degenerate bands in iron-pnictide superconductors [6]. The quadrupole-strain interaction brings about decreasing of the elastic constant, namely *softening*, with decreasing temperature. [7] The ultrasonic waves are now regarded as diagnosis tools for quantum states with the electric quadrupoles in solids.

Ever since the first observation of the low-temperature elastic softening of silicon wafer by means of ultrasonic diagnosis was reported [8], we have continuously investigated the physical properties of the vacancy in boron-doped silicon wafers using longitudinal ultrasonic bulk waves [9] and transverse bulk waves [10, 11], and surface acoustic waves (SAW) [12]. Common feature of considerable softening in the elastic constants in the boron-doped silicon wafers grown by the CZ method and floating zone (FZ) method ensures existence of the vacancy orbital with the electric quadrupoles. Furthermore, appreciable magnetic fields effects of the softening in the boron-doped wafers indicate the magnetism of the vacancy orbital accommodated odd number (three) electrons. In the present paper, we demonstrate recent progress of the ultrasonic diagnosis using the SAW as well as the bulk ultrasonic waves for the vacancy orbital in the boron-doped silicon wafers.

2. Softening of elastic constants

The dangling bonds of sp^3 orbitals ϕ_i ($i=1,2,3,4$) associated with a vacancy in the silicon lattice split into a singlet a_1 state at the energy of -3γ and a triplet t_2 state at γ due to kinetic energy $-\gamma = \langle \phi_i | H_0 | \phi_j \rangle$. The singlet a_1 state located beneath the top of the valence band accommodates two electrons with opposite spin orientation. The triplet state located near chemical potential accommodates one electron because the boron impurity state just above the top of the valence band accepts an electron from the triplet state. The spin $S = 1/2$ of the electron in the triplet state interacting to the orbit with $L = 1$. This spin-orbit interaction of $H_{so} = -\lambda \mathbf{L} \cdot \mathbf{S}$ bring about a ground state of Γ_8 quartet and an excited state of Γ_7 doublet at 1 K. Here, we adopt a spin-orbit coupling constant of $\lambda = 2/3$ K. The Γ_8 ground state with special unitary group symmetry $SU(4)$ possesses multipoles consisting of magnetic dipoles, electric quadrupoles and magnetic octupoles. [13] Among these multipoles, the electric quadrupoles conjugating to the external strains are measured by the elastic constants. This is similar to the fact that the magnetic dipoles coupled to the external magnetic fields are detected by the magnetic susceptibility. We refer the elastic softening of various Ce-based rear-earth compounds the Γ_8 ground states. [14]

In the present case of the softening on the silicon wafers, the electric quadrupoles O of the vacancy orbital couples to the appropriate elastic strains ϵ induced by the ultrasonic waves. The perturbation Hamiltonian of the quadrupole-strain interaction in unit volume of silicon lattice is written as

$$H_{QS} = - \sum_{i=1}^N g O(i) \epsilon \quad (1)$$

Here, $\sum_{i=1}^N$ means sum over vacancy sites in unit volume and N is number of the vacancies. g is a coupling constant of the quadrupole–strain interaction. The softening of the elastic constant of the silicon wafer caused by the Hamiltonian of equation (1) is explained as

$$C = C_0 - \frac{Ng^2\chi}{1 - g'\chi} \quad (2)$$

Here, C_0 is a background and g' is a parameter of inter-vacancy coupling. χ is the quadrupole susceptibility for the vacancy orbital with the Γ_8 (0 K) – Γ_7 (1 K) states. The orbital degeneracy of the Γ_8 quartet ground state in the vacancy orbital brings about the Curie-like term in the quadrupole susceptibility proportional to the reciprocal temperature, $\chi \sim 1/T$. This is the reason why the softening of silicon wafers emerges at low temperatures only. Therefore, low-temperature environment using ^3He – ^4He dilution refrigerators down to 20 mK is necessary for the ultrasonic diagnosis for vacancy evaluation of the silicon wafers.

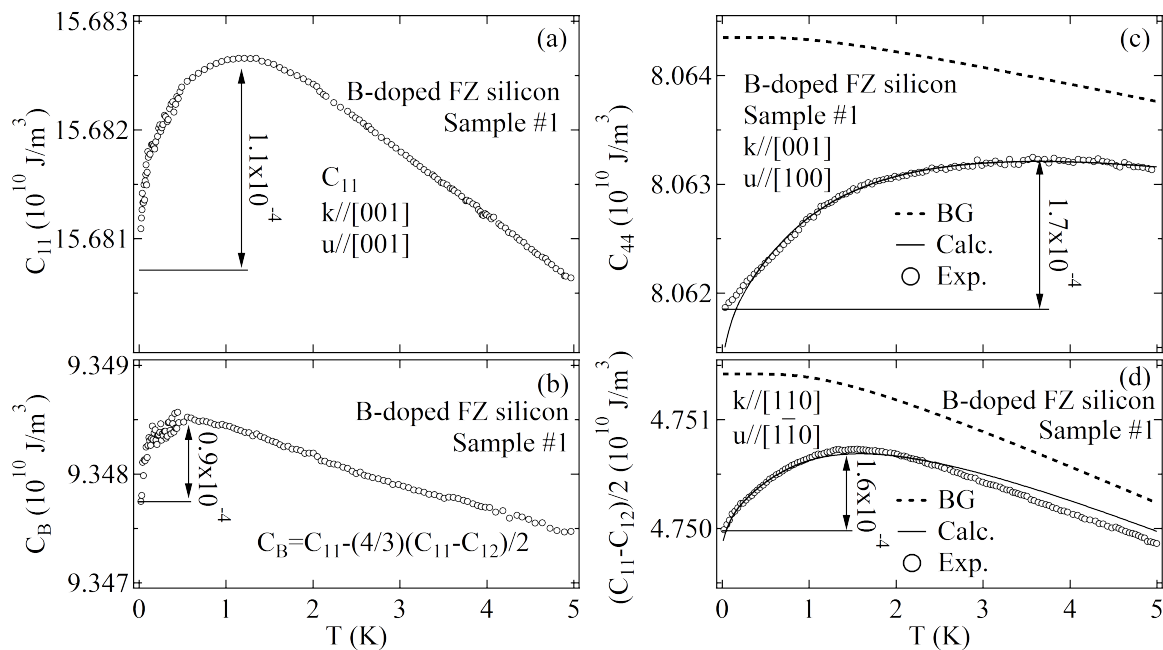


Figure 1. Temperature dependence of elastic constants C_{11} in (a), C_B in (b), C_{44} in (c), and $(C_{11} - C_{12})/2$ in (d) of boron-doped silicon wafers grown by a FZ method. [10]

The precise low-temperature ultrasonic velocity measurements below 10 K down to 23 mK on boron-doped silicon crystals were carried out. The elastic softening of the elastic constant $C_{L[111]}$ of the boron-doped silicon wafers measured by the longitudinal ultrasonic bulk waves along the $[111]$ direction was reported in reference [8]. The considerable magnetic field effects on the softening of the elastic constant $C_{L[111]}$ depending on the field direction was carefully investigated. [9] The softening of $C_{L[111]}$ and its magnetic field dependence were analyzed in terms of the quadrupole susceptibility of the electric quadrupole for the vacancy orbital with the Γ_8 (0 K) – Γ_7 (1 K) states.

The softening of the elastic constants of a boron-doped FZ silicon ingot was investigated by means of the bulk ultrasonic waves. [10] In figure 1, we show the low-temperature softening of the elastic constants C_{44} and $(C_{11}-C_{12})/2$ measured by the transverse waves in addition to the elastic constant C_{11} of the longitudinal waves. $C_B = (C_{11}+2C_{12})/3$ is the bulk modulus established by C_{11} and $(C_{11}-C_{12})/2$. The analysis of the softening based on the quadrupole susceptibility verified the Γ_8 (0 K) – Γ_7 (1 K) states of the vacancy orbital in the boron-doped silicon. The analysis gives a ratio of the coupling constant $g_{\Gamma_5}/g_{\Gamma_3} = 1.6$ for the two electric quadrupoles with different symmetries of Γ_3 and Γ_5 for the vacancy orbital. The theoretical study on the spin-orbit interaction [15] and electron phonon-interaction [16] reproduces the Γ_8 - Γ_7 states of the vacancy orbital in the boron-doped silicon.

It is supposed that the vacancy concentration distributes in the inner-space of the silicon ingot grown by the CZ method. The entropy term of the free energy of the electric furnace system with a non-equilibrium thermal distribution governs the distribution of the vacancy concentration. In slowly cooling process of the ingot in the furnace, the vacancies in excess amount condense into voids, which are regarded as “negative crystal”. The void has octahedral shape with 100 nm of typical size. Note that the void is frequently called as crystal originated particle (COP). As the pulling rate of the ingot is finely reduced, the void region changes to a neutral region, where mono-atomic vacancies are dominated but the void of the negative crystal is absent. The wafer taken from the void region in the ingot is used as a substrate for epitaxial wafer. The neutral wafer taken from the neutral region is widely used for memory device fabrication.

Some part of initially created vacancies condenses into voids and other part remains as mono vacancies in the silicon crystal. Using various samples taken from a boron-doped CZ ingot grown in GlobalWafers Japan, we carried out infrared laser light-scatterings to estimate number of the consumed vacancies N_{cons} for the void formation. The softening of the elastic constant of the concerned part of the ingot is caused by the residual vacancies with concentration N . As shown in the previous work [11], the distribution of the voids and the softening of C_{44} show position dependence in the ingot. Concerning with the samples in the center of neutral region, it is supposed that the number of the initially created vacancies N_{total} is explained by sum of the consumed vacancies N_{cons} and the residual vacancies N . [11] Utilizing the sum rule of $N_{\text{total}} = N_{\text{cons}} + N$, we deduced the one-to-one correspondence between the softening of C_{44} and the vacancy concentration N . Consequently, we obtained a coupling constant $g_{\Gamma_5} = 2.8 \times 10^5$ K of the quadrupole-strain interaction of $H_{\text{QS}} = -g_{\Gamma_5}O_{\text{zx}}\epsilon_{\text{zx}}$. This large deformation energy of $g_{\Gamma_5}\langle\Gamma_8|O_{\text{zx}}|\Gamma_8\rangle = 1.6 \times 10^5$ K = 14 eV for $\epsilon_{\text{zx}} = 1$ provides us the excellent ultrasonic diagnosis for the vacancy with small vacancy concentration. For example, the softening $\Delta C_{44}/C_{44} = 1.7 \times 10^{-5}$ in the transverse C_{44} wave of Fig. 1(c) of the FZ silicon is caused the vacancies with concentration $N = 5.2 \times 10^{13}$ cm⁻³. The coupling constant $g_{\Gamma_5} = 2.8 \times 10^5$ K of the vacancy orbital of silicon is quite large in comparing with $g \sim 10^2$ K of 4f-orbital in rare-earth compounds and $g \sim 10^3$ K of 3d-orbital in transition metal compounds. [16, 17] The theoretical analysis of the vacancy orbital in silicon gives enhanced electric quadrupoles due to an extended radius, which is consistent with the large quadrupole-strain interaction determined by the ultrasonic experiments. [18, 19] The deformation energy of 14 eV for the vacancy orbital due to the dangling bonds may be comparable to deformation potential about 15 eV for the electron band due to the host valence bonding in silicon. [20,21]

3. Surface acoustic wave

The evaluation of the vacancies in the surface layer of the silicon wafer is required in semiconductor industry, because the device fabrication makes most use the surface layer as the active region of the CMOS transistors. In order to respond this requirement, we develop the surface acoustic wave (SAW) diagnosis to detect the softening of the Rayleigh wave propagating on the silicon wafer. [12] Figure 2 schematically shows the inter-digital transducer (IDT) of Al electrodes with a comb gap $w = 2.5 \mu\text{m}$ fabricated on ZnO film deposited on the (001) surface of the silicon wafer. This IDT generates the SAW wave propagating along the [100] axis with a phase velocity of $v = 4967 \text{ m/sec}$. The observed wavelength of $\lambda = 9.37 \mu\text{m}$ for optimized resonance frequency of 515 MHz of the IDT agrees well with the designed wavelength of $\lambda = 4w \sim 10 \mu\text{m}$.

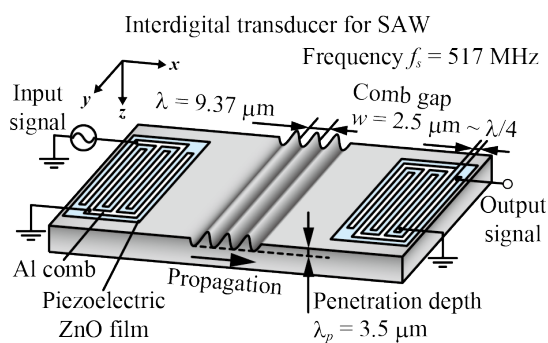


Figure 2. Schematic view of the interdigital transducer for surface acoustic wave (SAW) measurements on silicon wafer. [12]

Taking account of the null condition of the stress acting on the z -plane of the silicon wafer, we solved equation of motions of the SAW. The calculation gives the Rayleigh wave with the phase velocity of 4844 m/sec, which is consistent with the experimental observation of $v = 4967 \text{ m/sec}$. We obtained solutions of displacement vectors of u_x and u_z , which show an ellipsoidal trajectory motion in the z - x plane. The SAW propagates along the x -axis in penetrating into the z -axis within a penetration depth of $\lambda_p = 3.5 \mu\text{m}$. The elastic strains induced by the SAW consists of a volume strain ϵ_B with full symmetry, a tetragonal strain ϵ_u and orthorhombic one ϵ_v with Γ_3 symmetry, and a trigonal strain ϵ_{zx} with Γ_5 symmetry. The coupling of the symmetry breaking strains of ϵ_u , ϵ_v and ϵ_{zx} to the appropriate electric quadrupoles is relevant to describe the elastic softening of the SAW of the boron-doped silicon.

The low-temperature softening of the SAW on the boron-doped CZ silicon wafer is shown in figure 3. The softening of $\Delta C_s/C_s = 1.9 \times 10^{-4}$ below the onset of about 2 K down to the base temperature of 23 mK is caused by the coupling of the SAW to the vacancy orbital located in the surface layer within the penetration depth of $\lambda_p = 3.5 \mu\text{m}$. The distinct phase shift at 1.18K is due to the extrinsic effect at a superconducting transition point of the Al electrode used in the IDT. This phase shift is simply compensated by a smoothly jointing both sides. The solid line of figure 2 is a fit in terms of the quadrupole susceptibilities of the electric quadrupoles of O_u , O_v and O_{zx} of the vacancy orbital. Adopting the coupling constants of $g_{\Gamma_5} = 2.8 \times 10^5 \text{ K}$ and $g_{\Gamma_3} = 1.8 \times 10^5 \text{ K}$ of the quadrupole-strain interaction and appropriate background of C_s^0 indicated by a dashed line in figure 2, we deduce the vacancy concentration of $N = 3.1 \times 10^{12} \text{ cm}^{-3}$ within the penetration depth of $\lambda_p = 3.5 \mu\text{m}$ of the wafer concerned. This means that there exists one vacancy in the host lattice consisting of 10^{10} Si atoms. This amazing resolution is accounted for by the strong deformation energy 14 eV in the vacancy orbital to the surrounding silicon lattice.

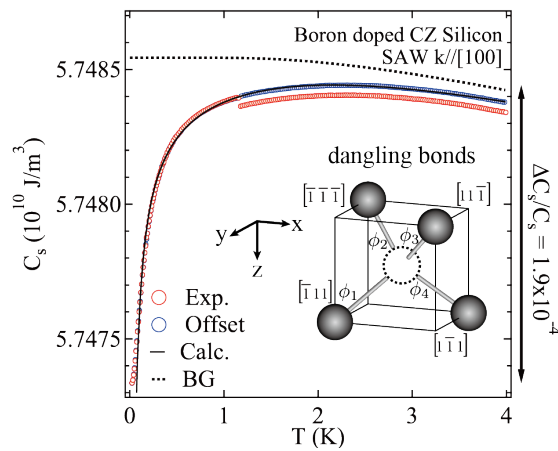


Figure 3. Temperature dependence of elastic constant C_s of the surface acoustic wave (SAW) of the boron-doped silicon wafer grown by a CZ method. [12]

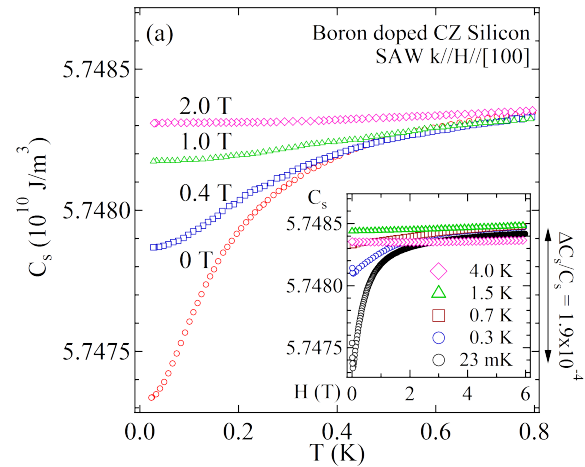


Figure 4. Temperature dependence of the elastic constant C_s of the SAW on the boron-doped silicon wafer under applied magnetic fields. Inset shows the magnetic field dependence of C_s at low temperatures. The magnetic fields were applied along the $[100]$ axis parallel to the propagation direction of the SAW. [12]

The measurements of the magnetic field dependence of the softening of the elastic constant C_s of the SAW is important to examine the magnetism of the vacancy orbital with the $\Gamma_8 - \Gamma_7$ states. As is shown in figure 4, the low-temperature softening observed below 0.8 K down to 23 mK in the zero field is considerably reduced with increasing field above 0.4 T up to 2.0 T. Here, the magnetic fields were applied along the $[100]$ axis parallel to the propagation direction of the SAW. The inset of figure 4 shows the magnetic field dependence of the elastic constant C_s of the SAW at low temperatures. The relative change of $\Delta C_s/C_s = 1.9 \times 10^{-4}$ with increasing the fields of up to 6 T at the base temperature of 23 mK well agrees with the amount of the softening in the zero field of figure 3. In the increased temperature of 0.3 K, the change of the field dependence is reduced very much because of the thermal population of the lifted states in the fields. The high temperature of 4.0 K smeared out the distinct field dependence observed in the base temperature of 23 mK. The theoretical analysis in terms of the quadrupole susceptibility for the $\Gamma_8 - \Gamma_7$ states of the vacancy orbital successfully explained the experimental observations in figures 3 and 4.

4. Conclusion

The ultrasonic diagnosis using the SAW as well as the conventional bulk ultrasonic waves successfully observed the considerable low-temperature softening of the elastic constants caused by the vacancies in silicon wafers currently used in semiconductor device fabrication. The magnetic field dependence of the low-temperature softening is accounted for by the $\Gamma_8 - \Gamma_7$ states of the vacancy orbitals with the magnetism. The strong quadrupole-strain interaction enables us to observe the vacancy with very small concentration of $N \sim 10^{12} \text{ cm}^{-3}$. The SAW diagnosis in particular is powerful to evaluate the vacancies located in the surfaced layer of the silicon wafer. The continuous pursuing of highly density devices with gate size beyond 19 nm requires the vacancy controlling in device

fabrication processes. We wish to develop the SAW diagnosis as an innovative technology for the evaluation of the vacancy in the active region of the silicon wafer.

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