

Vacancy Formation Energy of Silicon Determined by a New Quenching Method

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(Received June 7, 2001; accepted for publication July 11, 2001)

By applying a new quenching method, we determined the formation energy of vacancies in high-purity silicon. Specimens were heated in H₂ gas at high temperatures for 1 h followed by quenching in water. By this method, vacancies are quenched in the form of complexes with hydrogen and the vacancy formation energy can be determined from the quenching temperature dependence of the intensity of the optical absorption peak due to the complexes. The vacancy formation energy of silicon was determined to be about 4.0 eV. This value is in good agreement with results of recent theoretical calculation.

KEYWORDS: vacancy, formation energy, hydrogen, optical absorption, silicon

From both practical and basic points of view, it is increasingly important to clarify the properties of vacancies (V) existing at high temperatures in silicon. With increasing miniaturization of silicon devices, secondary defects such as voids and swirls which are formed during crystal growth by agglomerations of V are known to have harmful effects on device performance. To understand the agglomeration process and to prevent it, it is necessary to know the properties of V. From a basic-research point of view, determination of the V formation energy has been a critical issue since the 1960s. Theoretical estimation has been performed every time a new calculation technique has been developed.¹⁾ Experimental results obtained by *in situ* measurements, however, have been contradictory.^{2–4)} Until now, two kinds of *in situ* methods, i.e., positron lifetime measurement and measurements of length and lattice parameter have been applied to the study of point defects in silicon at high temperature. Dannefaer *et al.*²⁾ determined the V formation energy in silicon to be 3.6 ± 0.2 eV from positron-lifetime measurements at high temperatures using internal positron source (²²Na). Following their work, Würschum *et al.*³⁾ performed similar study using an MeV positron beam. They, however, observed no substantive change in the positron lifetime up to the melting point of silicon. Furthermore, Throwe *et al.*⁴⁾ also found no evidence of positron trapping at thermally generated V in Doppler-broadening and diffusion length for temperatures up to the melting point. On the other hand, Okada determined the net concentration of dominant native defects in a floating-zone grown silicon crystal at high temperatures from the difference in temperature dependences of specimen length and lattice constant.⁵⁾ In his experiment, the V formation energy was not determined since the temperature dependence of the net concentration of native defects (V-I, I:self-interstitial) was not simple.

To study point defects in thermal-equilibrium in silicon, we applied a quenching method instead of the above-mentioned *in situ* methods. The quenching method itself is very useful and successful in the case of metals. It is, however, difficult to apply to silicon since silicon is easily contaminated by impurities at high temperature and the migration energy of V in silicon is very small (< 0.45 eV).^{6,7)} It is well known that quenched-in defects have been identified as Fe by means of EPR measurement.⁸⁾ Due to their small migration energy, a V easily comes out to the specimen surface or forms complexes which are difficult to detect during quenching. To quench

isolated V, the quenching speed should be much faster than 10^5 K/s, which is too high to prevent specimen breakage. To overcome this difficulty, we applied a new quenching method. In this method, quenching is performed in an H₂ gas and therefore V are quenched as H-V complexes which are detected by optical absorption due to the localized vibrational mode of H included in the complexes.^{9–11)}

In this Letter we report a new approach for determination of the V formation energy in high-purity silicon. The value determined by applying the new quenching method is in good agreement with recent theoretical values. Moreover, from comparison of the above result with previous results, we show that the V formation energy is sensitive to doped impurities.

We prepared specimens from a high-purity silicon (n-type) crystal. The carrier concentration at room temperature (RT) was about 4×10^{12} cm⁻³. The specimens were sealed in quartz capsules together with H₂ gas and heated at 1200–1390°C for 1 h, followed by quenching in water. The optical absorption peaks were observed at 5 K by a Fourier transform infrared spectrometer. The thickness of a specimen was about 12 mm and the spectral resolution was 0.25 cm⁻¹. Isochronal annealing was carried out for 30 min at various temperatures in the range of 100–650°C.

Representative optical absorption peaks observed after quenching are shown in Fig. 1. When specimens were quenched from 1300°C, the optical absorption peaks due to H₂¹²⁾ and H₂^{*13)} were observed at about 3618.6 (abbreviated as 3619 hereafter) cm⁻¹ and 1838.7 (1839) & 2062.1 (2062) cm⁻¹. The intensity of the H₂^{*} absorption peak was much smaller than that of the H₂ absorption peak. When quenched from 1390°C, five peaks were observed at about 2131.5 (2132), 2191.8 (2192), 2202.7 (2203), 2220.8 (2221) and 2222.9 (2223) cm⁻¹, in addition to optical absorption peaks due to H₂ and H₂^{*}. To simplify the description of the peak, we use values in parentheses hereafter. The 2223 cm⁻¹ peak has been assigned to the Si-H stretching mode of V saturated with four H atoms (VH₄).^{14,15)} From this, it is definitely confirmed that V are quenched in the form of H-V complexes. The existence of H-V complexes in a quenched specimen is due to two factors: the complex-formation reaction between H and V is very fast and the thermal stability of the complexes is also high.

The annealing behaviors of the 2192, 2203, 3619 and 2223 cm⁻¹ peaks are shown in Fig. 2. The annealing behaviors of these peaks at above 350°C show that the 2192 and

2203 cm^{-1} complexes are transformed to the 2223 cm^{-1} complexes by the reaction with H_2 . Namely, the intensity of the 2223 cm^{-1} peak increases with the decrease of intensities of the first three peaks at above 350°C . Incidentally, at temperatures between 100 and 350°C , the intensities of the 2192 and 2203 cm^{-1} peaks increase and that of the 3619 cm^{-1} peak decreases. These results strongly suggest both the existence of "hidden" V-H complexes which are not detected by optical absorption measurement and the transformation of these hidden complexes to the 2192 and 2203 cm^{-1} complexes. Based on the annealing behaviors of the 2192 and 2203 cm^{-1} peaks shown in Fig. 2 and our previous results about their quenching temperature dependence,¹⁰⁾ we have assigned the two peaks

to a VH_3 complex with different vibrational modes. As for the complexes responsible for these two peaks, another model has been proposed,¹⁴⁾ namely, a V_2H_6 complex. This model¹⁴⁾ was proposed in a study of proton-implantation experiment. Contrary to proton-implantation, local concentrations of vacancy in quenched specimens seem to be very low. Hence, the probability of V_2H_6 complex formation is very small and we do not adopt the V_2H_6 model. The formation reactions of H-V complexes are thought to strongly depend on the quenching condition. The result of Fig. 1 shows that the VH_3 complex is predominant in as-quenched specimen.

We interpret the annealing temperature dependence of the 2192 , 2203 , 3619 , and 2223 cm^{-1} peaks by the following explanation assuming the hidden complexes to be VH and/or VH_2 . Indeed, we have been able to observe an optical absorption peak due to one of the hidden complexes, namely, the VH_2 complex in quenched silicon doped with carbon and H, where V concentration was higher than that in high-purity silicon (Fig. 4). The increase of the 2192 and 2203 cm^{-1} peaks intensities at temperatures between 100 and 350°C is due to the formation of the VH_3 complex by reactions between a VH complex and an H_2 (3619 cm^{-1}) or a VH_2 complex and an H which is dissociated from H_2 . The decrease of the 2192 and 2203 cm^{-1} peaks intensities and the increase of the 2223 cm^{-1} peak intensity above 350°C is due to the formation of the VH_4 complex by a reaction between the VH_3 complex and H_2 or the VH_3 complex and an H. As already described, the 2221 cm^{-1} peak was also observed. The annealing behavior of this peak shows that the 2221 cm^{-1} complex is also transformed into the VH_4 complex.

As shown in Fig. 2, almost all H-V complexes are transformed into only one complex, the VH_4 complex, by annealing at 450°C . Hence, it is considered that the V concentration is proportional to the peak intensity of the VH_4 complex. From this, it is possible to determine the V formation energy of silicon without determining the absolute value of V concentrations. Based on Fig. 2, we annealed specimens quenched from various temperatures at 450°C and then determined the relative concentrations of V from the intensities of the 2223 cm^{-1} peak. Figure 3 shows some spectra of spec-

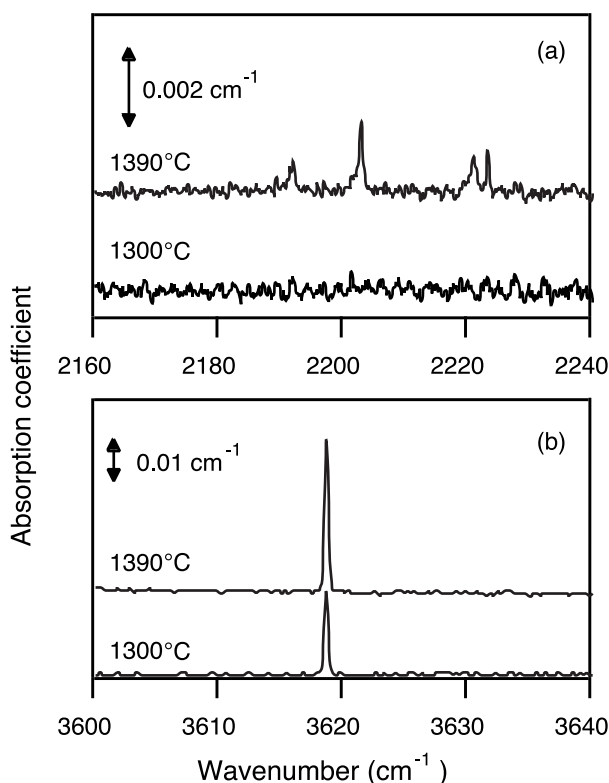


Fig. 1. Optical absorption peaks observed in high purity silicon heated at 1300°C and 1390°C for 1 h in an H_2 gas atmosphere followed by quenching in water.

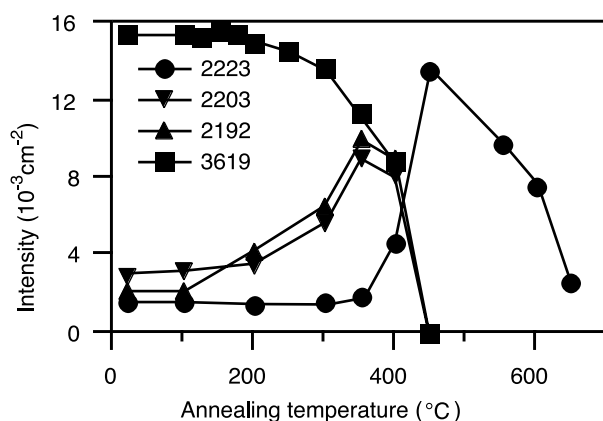


Fig. 2. The isochronal annealing temperature dependence of the integrated intensities of the 2192 , 2203 , 2223 , and 3619 cm^{-1} peaks. The specimen was quenched from 1390°C .

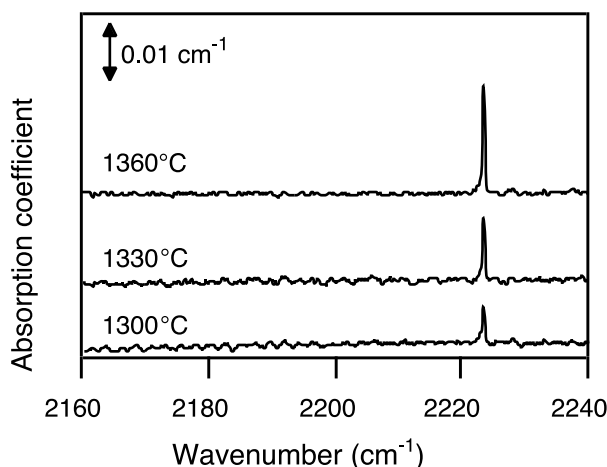


Fig. 3. The quenching temperature dependence of the 2223 cm^{-1} peak observed in specimens heated at 1300°C , 1330°C , and 1360°C for 1 h in an H_2 gas atmosphere followed by quenching in water and subsequent annealing at 450°C for 0.5 h in an argon gas.

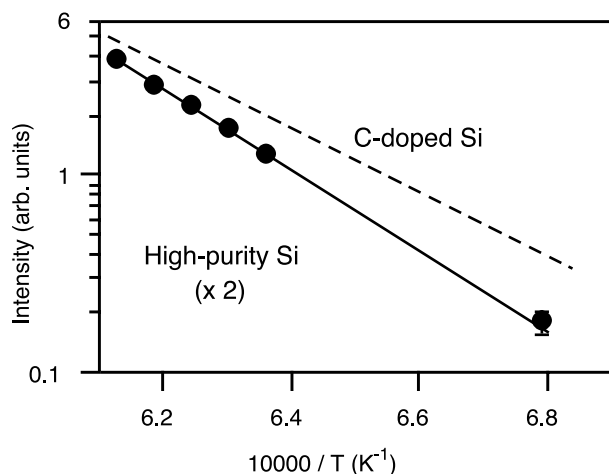


Fig. 4. The quenching temperature dependence of the integrated intensities of the 2223 cm^{-1} peak observed in high-purity silicon (solid line) and in C-doped silicon (dashed line).

imens quenched from various temperatures and annealed at 450°C . The 2223 cm^{-1} peak is strong enough to determine the relative concentrations of the VH_4 complex and consequently the formation energy of V. From the Arrhenius plot shown in Fig. 4, the formation energy of the VH_4 complex and consequently that of V is determined to be about 4.0 eV . Recently, the V formation energy of silicon has been calculated to be about 3.0 to 4.5 eV depending on methods of calculation.¹⁾ These values are in good agreement with our result, confirming the usefulness of our new method of quenching V in silicon in the form of a V-H complex.

Another important result is derived by comparison this result with our previous results of C- or Au-doped silicon,^{9,11)} namely, the formation energy of V depends on doped impurities. The formation energy of V in C- or Au-doped silicon is lower than that in intrinsic silicon, 3.2 eV ¹¹⁾ and 2.1 eV ⁹⁾ in C-doped and Au-doped silicon, respectively. The result obtained in C-doped silicon is shown in Fig. 4 in addition to that in high-purity silicon. These values are close to the activation energies of the diffusion of C and Au in silicon, which have been reported to be about 3.04 eV ¹⁶⁾ and $1.7\text{--}2.04\text{ eV}$,^{17,18)} respectively. Further work is now in progress to clarify the impurity dependence of the formation of V in silicon.

Besides, the results shown in Fig. 4 seems to cast doubt on the common assumption among semiconductor researchers that the multiplication ($[\text{V}] \cdot [\text{I}]$) of concentrations of V ($[\text{V}]$) and I ($[\text{I}]$) is constant and does not depend on the dopants.¹⁹⁾ This is so far a very important concept and is often used to explain high temperature phenomena related to point defects such as diffusion in silicon. According to Fig. 4, $[\text{V}]$ in C-doped silicon is higher than that in high-purity sili-

con. Incidentally, it is well-known that the I concentration in C-doped silicon is also higher than that in high-purity silicon because C has a smaller covalent radius than silicon. Experimental evidence for the high concentration of I is the high density of interstitial-type dislocation loops in C-doped silicon.²⁰⁾ Hence, $[\text{V}] \cdot [\text{I}]$ in C-doped silicon is larger than that in high-purity silicon.

In conclusion, the formation energy of V in high-purity silicon was determined to be about 4.0 eV with our new quenching method. This value is in good agreement with recent theoretical values. Our new quenching method opens up a new way to determine the formation energy of V in various silicon crystals. Application of this method to Czochralski-grown silicon is highly expected to clarify the void formation mechanism and to lead to new ways of reducing the void density.

This work was partly supported by the JSPS Research for the Future Program under the project "Ultimate Characterization Technique of SOI Wafers for Nano-scale LSI Devices" and a Grant-in-Aid for Scientific Research on Priority Areas A of 'New Protium Function' from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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