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Anharmonic vibrations of the dicarbon antisite defect in 4H-SiC

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Dicarbon antisite defects were created by either electron irradiation or ion implantation into 4H-SiC. The no-phonon lines from the dicarbon antisite defect center were observed with their phonon replicas. The stretch frequencies of the defect were observed up to the fifth harmonic. The Morse potential model accounts for the anharmonicity quite well and gives a very good prediction of the vibration energies up to the fifth harmonic with an error of less than 1%. First principles calculations show that the model of a dicarbon antisite defect along with its four nearest neighboring carbon atoms can explain the observed anharmonicity. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3699269]

As a wide bandgap semiconductor, SiC has attracted a lot of research interest in recent decades. It has high electron mobility, high breakdown electric field, and high thermal conductivity. All these make it suitable for electronic use under high temperature, high frequency, and high power conditions. Different impurities and defects in SiC have been studied for decades. Recently, Steeds *et al.* reported a triplet of no phonon lines and their vibrational replicas in 4H-SiC after electron irradiation.[1] By comparing the experimental results to the published results of *ab initio* local density approximation (LDA) calculations by two groups,[2,3] the authors conclude that the triplet lines are associated with dicarbon antisite defects in 4H-SiC. In the previous work from our group,[4] we reported the no-phonon and phonon replica lines and issues associated with the dicarbon antisite defect by studying the creation and annealing behavior at different temperatures.

In this letter, we report that (i) the dicarbon antisite phonon replicas up to the fifth harmonic have been observed by low temperature photoluminescence (LTPL), (ii) the Morse potential model accounts for the observed anharmonicity, and (iii) the potential energy surface for the stretch vibration calculated from first principles is surprisingly well described by the Morse potential and, by making an appropriate choice for the value of the effective reduced mass, the Morse potential obtained from a fit to the data agrees very well with the calculated potential.

All the samples used in this study were very carefully characterized 15–20 μm thick 4H-SiC epitaxial layers.[5] Some were intentionally n-type or p-type doped (doping: 2–4×10^{15} cm^{-3}), others were non-intentionally doped, and the doping was not measured. 170 keV and 1 MeV electron irradiations were carried out at fluences of 10^{15} cm^{-2} to 5×10^{16} cm^{-2}. The samples were put on a water-cooled plate during electron irradiation to avoid heating. The H$^+$ and

^{4}He$^+$ bombardments were at the 5×10^{10} cm^{-2} fluence level. The samples were annealed in Ar for 30 min at temperatures between 700 °C and 1700 °C with 100 °C intervals. Temperatures were raised directly from room temperature to the desired temperature for every individual sample. A particular sample was annealed only once, so a large number of identical samples were used for this study. The LTPL measurements were carried out at 2 K using an immersion type liquid He cryostat. A frequency doubled argon ion (FreD) laser at 244 nm wavelength at an excitation power of 40 mW was used as the excitation source. The luminescence was dispersed in an asymmetric Czerny-Turner spectrometer and collected with a liquid nitrogen cooled charge-coupled device (CCD) array with approximately 0.1 meV resolution.

In Fig. 1 and Table I, we show the phonon replicas observed for the triplet no-phonon lines a_0, b_0, and c_0, where the subscript 0 indicates a no-phonon line, and H$_n^a$ indicates the nth harmonic of the high-energy local vibrational modes of a_0. The slit size was 100 μm. In Table I, ΔE^{ph}_{3-2}, for example, is the additional vibrational energy (third vibrational quantum) contributing to the third replica, relative to the second replica. The a_0, b_0, c_0 lines have first order phonon replicas of about 132 and 180 meV. However, for the second harmonic replicas a combination of the 132 and 180 meV modes is also observed. Especially note-worthy is the observation of five harmonics for the a_0 line with decreasing energy, indicating anharmonicity. The theoretical calculations show that the high energy local vibrational mode can be interpreted as due to the stretching vibration of the C-C dumbbell in the dicarbon antisite $(C_2)_{Si}$. Therefore, we can treat the C-C dumbbell as an anharmonic diatomic configuration using the Morse potential,[6] assuming that the interaction with the rest of the lattice can be built into the parameters. For a Morse potential, the energy spacing between two consecutive energy levels decreases with increasing vibrational quantum number. The difference between adjacent energy spacings is a constant. Using the first two energy spacings observed in Fig. 1, we calculated the two

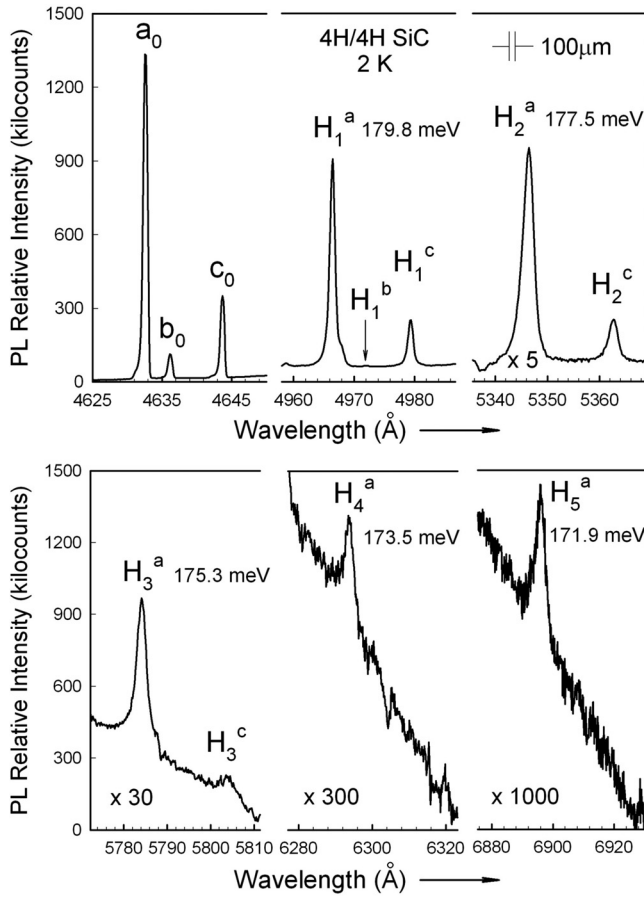a)Current address: Applied Materials, Inc., Santa Clara, CA, USA. Electronic mail: feiyan@gmail.com.

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FIG. 1. Triplet no-phonon lines a_0, b_0, c_0 and the high-energy local vibrational modes of a_0 up to the fifth harmonic.

TABLE II. A comparison of experiment and Morse potential predictions for the harmonic energies up to the fifth order of the dicarbon antisite C-C dumbbell vibrations in 4H-SiC.

Triplet line a	ΔE_{10} (meV)	ΔE_{21} (meV)	ΔE_{32} (meV)	ΔE_{43} (meV)	ΔE_{54} (meV)
Experiment	179.8	177.5	175.3	173.5	171.9
Morse potential Prediction	–	–	175.2	172.9	170.6

levels at the same time. We applied a plane wave cutoff of 420 eV with the projector augmented wave (PAW) method and density functional theory within the LDA(Ref. [7]) to calculate the total energies and forces. We utilized the VASP code for the calculations.[8] We optimized the full geometry until the forces were below the given threshold. We note that the symmetry of the defect is C_{1h} in 4H-SiC, but the local symmetry resembles the D_{2d} symmetry in a 3C-SiC crystal. The vibrational modes within the quasi-harmonic approximation were calculated as the numerical derivative of the forces. We applied a defect-molecule model in the calculation of vibrations: either (i) C1 and C2 atoms or (ii) C1 to C6 atoms were allowed to vibrate (see Fig. 2). The calculated stretch mode energy in the case (i) was about 172 meV, which slightly increased to 174 meV in the case (ii). In the case (ii), we obtained 136 meV for the symmetrically allowed bending mode that can be tentatively compared to the experimental value of 132 meV. Based on our previous results, we believe that the main reason for the discrepancy between the calculated (174 meV) and measured (~180 meV) stretch modes is due to the limitation on the number of atoms that were allowed to vibrate and that the LDA potential energy surface (PES) is sufficiently appropriate. In this study, we aim to understand the anharmonicity of the stretch mode. We found for both cases (i) and (ii) that the normal coordinates of the stretch mode show the motion of C1 and C2 atoms along their bond. This enables a simplification of the description of the stretch mode to a one-dimensional model where only C1 and C2 atoms are moving symmetrically with respect to their bond center by compressing or expanding the bonding distance between them. We mapped the PES at 17 points where the maximum compression (expansion) of the bond was about 0.24 (0.36) Å. We obtained a very accurate fit of a Morse potential to the calculated first principles data despite the fact that the Morse potential contains only two parameters. A comparison of the

parameters associated with a Morse potential fit. Then we calculated the energies of the third, fourth, and fifth order vibrational modes. The results from the Morse potential predictions and the experimental results from LTPL measurements are listed in Table II. We can see that they agree well within an error of less than 1.3 meV up to the fifth harmonic, which is just 0.8% in error.

The proposed model of the PL centers is the dicarbon antisite defect.[1] For the first principles calculations, we focus our investigation particularly on the high-spin (S = 1) configuration at the hexagonal site in 4H-SiC. This defect is modeled in a large 576-atom supercell using the Γ-point for K-point sampling that ensures both the convergent charge density and the monitoring of the (quasi) degenerate defect

TABLE I. "Dumbbell" center triplet no-phonon lines with phonon replicas. ΔE^{ph}_{1-0} is the additional vibrational energy (first vibrational quantum) contributing to the first replica relative to the no-phonon line. ΔE^{ph}_{2-1} is the additional vibrational energy (second vibrational quantum) contributing to the second replica relative to the first replica and similarly for ΔE^{ph}_{3-2}, ΔE^{ph}_{4-3}, and ΔE^{ph}_{5-4}.

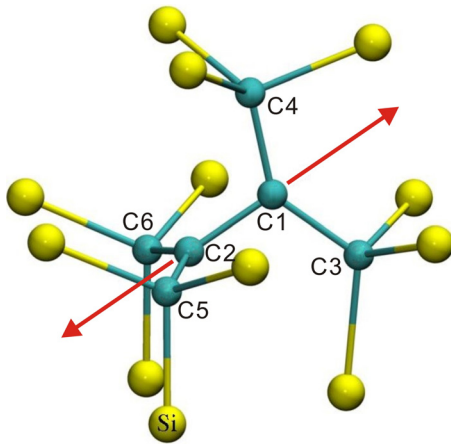| No-phonon lines (Å)	ΔE^{ph}_{1-0} (meV)	ΔE^{ph}_{2-1} (meV)	ΔE^{ph}_{3-2} (meV)	ΔE^{ph}_{4-3} (meV)	ΔE^{ph}_{5-4} (meV)
a_0 4632.46	179.8	177.5	175.3	173.5	171.9
b_0 4635.79	180.7				
c_0 4643.51	180.0	177.9	175.5		
a_0 4632.46	132.4	132.5			
b_0 4635.79	132.3				
c_0 4643.51	131.4	131.3			
a_0 4632.46	132.4	179.9	177.6	175.0	
c_0 4643.51	131.4	180.0	178.2	175.2	

FIG. 2. Dicarbon antisite defect at the hexagonal site in 4H-SiC. Carbon atoms C1 and C2 form the "dumbbell" mentioned in the text. The carbon atoms are labeled by numbers. The arrows indicate the motion of atoms C1 and C2 in the stretch vibration mode.

FIG. 3. Plots of both the Morse potential fit and the potential obtained from first principles calculation.

Morse potential fit and the first principles calculation is shown in Fig. 3. This one-dimensional Morse potential can be applied in the one-dimensional Schrödinger equation where the kinetic energy contains the effective reduced mass (μ) of the vibrating system. If the C1 and C2 atoms did not connect to the rest of the SiC crystal then $\mu = m_C/2$, where m_C is the mass of the ^{12}C isotope. However, μ will be reduced due to the fact that C1 and C2 atoms are bound to the rest of SiC crystal, so $\mu = \chi m_C/2$, where $\chi < 1$. We used μ as a parameter to fit the first transition to the experimental value of 179.8 meV. For this choice, we found that reduced mass μ value of 9983.939635 a.u. would fit the data and $\chi \approx 0.9$, which is physically reasonable.

In summary, we have been able to obtain a surprisingly sharp and detailed spectrum of the vibrational modes of the dicarbon antisite defect in 4H-SiC up to the fifth harmonic. It is possible to obtain a Morse potential fit to our data which, using positions of the first two harmonics, predicts harmonics 3, 4, and 5 to an accuracy of better than 99%. Fortunately, first principles 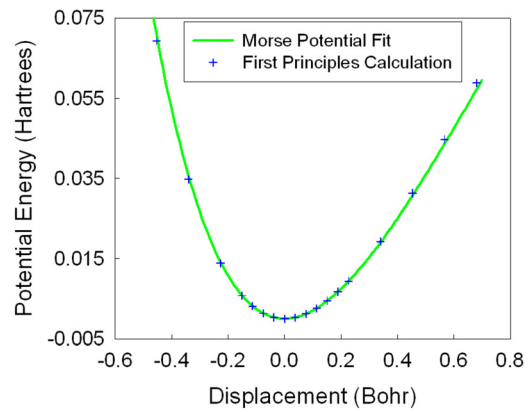calculations of vibrational modes are quite accurate and reliable, and we have used such calculations to obtain theoretical values of the mode frequencies for our dicarbon antisite. The agreement between theory and experiment is very good, giving us great confidence in the assignment of our observed defect in 4H-SiC to the dicarbon antisite, one of the few defects in SiC which is now fairly well understood.

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