Tunneling states in neutron-disordered bulk silicon

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Measurements of the variation of the low-temperature (LT) ultrasonic velocity and Raman scattering spectroscopy were performed on pure, bulk single-crystalline silicon, both unirradiated and irradiated with fast-neutron doses up to 1.7 and 3.2×10^{21} n/cm^2 ($E>0.1$ MeV). This irradiation is found to transform the crystalline silicon structure into a partly disordered state. Previous LT studies on amorphous and partly disordered low-coordinated solids show the presence of low-energy excitations, which can be described as quantummechanical tunneling states (TS's). The possible ''glassy'' behavior of highly coordinated solids, is, however, still under discussion. Our observations indicate the presence of TS in neutron-irradiated bulk silicon. This result makes it possible to study TS in highly coordinated bulk solids. [S0163-1829(98)07735-2]

At low temperatures amorphous and partly disordered solids show thermal, dielectric and acoustic properties that are different from those in their crystalline counterparts. A theoretical description of these universal anomalies was put forward by the tunneling model (TM).[1,2] This model explains the so-called ''glassy'' anomalies by the existence of low-energy excitations, or tunneling states (TS's), which are characterized by a broad distribution of energies and relaxation times. The tunneling model describes all dynamic properties, but it is restricted to low temperatures and it is purely phenomenological, giving no indication for the microscopic origin of the TS.

In search of a microscopic origin of TS, an extensive study of neutron-irradiated quartz[3] shows that following neutron irradiation, glassy anomalies are induced. It also revealed an anistropic behavior of the TS, leading to a description of TS as a rotation of coupled SiO_4 tetrahedra. This implies that the presence of TS needs to be accompanied by a certain degree of freedom, which is in agreement with the belief that TS can only be hosted by solids with a low average coordination of the individual atoms. To elucidate the question whether these TS can also be present in topologically higher constrained solids, the study of partly disordered or amorphous silicon is of interest.

Reports of TS in the mechanical properties of single crystalline Si have been made by Kleiman, Agnolet, and Bishop,[4] claiming a major revision to the tunneling state theory to explain the low-temperature regime. However, an alternative analysis of his results shows that the observed effects are most probably due to impurities in the crystal.[5]

Glassy anomalies have already been reported in certain amorphous silicon films,[6–8] but it is believed that the effects were due to voids[8] and low-density regions[7] that are unavoidable side effects in the sputtered films. Recently, Liu *et al.*[9] reported on amorphous solids without low-energy excitations. They showed that adding small concentrations of hydrogen virtually eliminates the low-energy excitations in low-pressure hot-wire-assisted chemical vapor deposited (HWCVD) amorphous silicon films. The existence of TS in tetrahedrally bonded amorphous networks has also been investigated on thick amorphous germanium films by Duquesne and Bellessa.[10] They claim that TS do exist in these highly coordinated amorphous materials and explain the contradictory conclusions of previous experiments performed on a-Ge or a-Si by either a lack of sensitivity or by the unsuitability of the used experimental methods.

In order to contribute to this discussion concerning the presence of TS in amorphous silicon, we started an ultrasonic study on neutron-irradiated silicon. One of the effects resulting from this high-energy neutron irradiation is the introduction of large regions that contain displaced atoms. Due to the presence of such structural damage the crystal can become partly amorphous. The volume fraction of these amorphous regions increases with the irradiation dose. Hence, we can use neutron-irradiated silicon as a model for the completely amorphous state. To avoid the consequences of sputtered amorphous films, we used bulk single-crystalline Si as a starting material for our experiments. The aim of this study is to investigate whether fast-neutron irradiation can induce TS in bulk single-crystalline silicon, in spite of its high coordination. We will report on ultrasonic velocity measurements and Raman spectroscopy performed on pure single-crystalline silicon and on silicon irradiated with different neutron doses. We will demonstrate that our data include no evidence for TS in pure single-crystalline silicon and that due to neutron irradiation an additional effect is introduced in the changes in ultrasonic velocity.

Our data will be analyzed in the framework of the tunneling model (TM). This model describes TS as atoms or groups of atoms which can tunnel in a double, asymmetric potential well. The energy difference between the eigenstates is given by $E=\sqrt{\Delta^2+\Delta_0^2}$, where Δ represents the asymmetry of the potential well. Δ_0 is the tunnel splitting that can be written as $\Delta_0=\hbar\Omega\exp(-\lambda)$, where λ describes the overlap of the wave functions. $\hbar\Omega/2$ is the ground-state energy of the particle in an isolated well. The tunneling model also assumes that Δ and λ are independent of each other and that they have a uniform distribution: $P(\Delta,\lambda)d\Delta d\lambda=\bar{P}d\Delta d\lambda$, where $\bar{P}$ is a constant and represents the density of states of

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the TS. To describe the effect of the TS on the low-temperature ultrasonic properties, two different mechanisms have to be considered: the resonant and the relaxation processes. Resonant absorption occurs by those TS having an energy splitting E corresponding to the phonon energy $E=\hbar\omega$. At the lowest temperatures, where $\hbar\omega \ll kT$, this process leads to a frequency-independent but temperature-dependent change of the sound velocity, given by[11]

$$\frac{v(T)-v(T_0)}{v(T_0)}=C\ln\frac{T}{T_0}=\frac{\bar{P}\gamma_l^2}{\rho v_l^2}\ln\frac{T}{T_0}, \qquad (1)$$

where T_0 is an arbitrary reference temperature and γ_l represents the coupling of the TS to the longitudinal phonons. At higher temperatures, the TM predicts a logarithmic decrease:[11]

$$\frac{v(T)-v(T_0)}{v(T_0)}=-\frac{C}{2}\ln\frac{T}{T_0}=-\frac{\bar{P}\gamma_l^2}{2\rho v_l^2}\ln\frac{T}{T_0}. \qquad (2)$$

For our experiments we used pure, bulk single-crystalline silicon. The main impurities are O ($\sim 10^{17}$ cm^{-3}), P (2×10^{16}–5×10^{15} cm^{-3}) and C ($<5\times10^{16}$ cm^{-3}). The samples are cylindrically shaped and have a diameter of 3 mm and a length of 15 mm. The rod axis is parallel to the [100] direction. The fast-neutron irradiation is performed in the BR2 reactor of the Belgian Nuclear Research Center (SCK•CEN). The effective irradiation time to obtain fast-neutron doses ($E>0.1$ MeV) of 1.7×10^{21} n/cm^2 (sample labeled Si-2) and 3.2×10^{21} n/cm^2 (sample Si-4) is 42 and 78 days respectively. The samples were positioned inside a fuel element of the core of the reactor. They were loaded into an aluminum irradiation capsule filled with He gas to reduce the temperature increase due to the γ heating under irradiation. A good thermal contact between the irradiation capsule and the primary cooling water was also provided. Nevertheless, the calculated maximum temperature in the center of the silicon during the irradiation was 150 °C.

The high-energy collisions lead to cascade processes, resulting in large regions of displaced atoms which may be amorphous. In general, these regions are considered to be spherical, with a radius of the order of 100 Å,[12] where a center of vacancies is embedded in a region of interstitials. According to Schröder, Wild, and Minninger[13] elastic collisions between neutrons and silicon atoms create displacement clusters that start to overlap for sufficiently high neutron doses, resulting in a highly disordered crystal hosting defect complexes. Further overlap is said to turn the silicon into an amorphous state. Due to the large mean free path of fast neutrons in silicon the cascade damage associated with the atomic collisions is homogeneous throughout the sample. The number of the cascades depends on the irradiation dose. The mass density of the samples was measured using a hydrostatic method and this resulted in 2.333 ± 0.004 g/cm^3 for the unirradiated sample and 2.326 ± 0.001 and 2.327 ± 0.002 g/cm^3 for Si-2 and Si-4 respectively.

Previously reported Raman scattering data[14] on the same samples used in the current study give evidence that the irradiation has caused the crystalline structure to become partly amorphous. This is shown by the emergence of an amorphous band at 483 cm^{-1} in the Raman spectra of the irradiated samples that becomes more pronounced with increasing dose. However, the crystalline peak at 520 cm^{-1} is still present for the highest dose studied. By comparing the intensities of the crystalline and the amorphous band, an estimation was made of the volume fraction of the amorphous regions. From the ratio between the integrated intensities of the amorphous and crystalline Raman modes, we calculated the values for the amorphous volume fraction in Si-2 and Si-4 to be a minimum of 2.7 and 4.1 %, respectively.

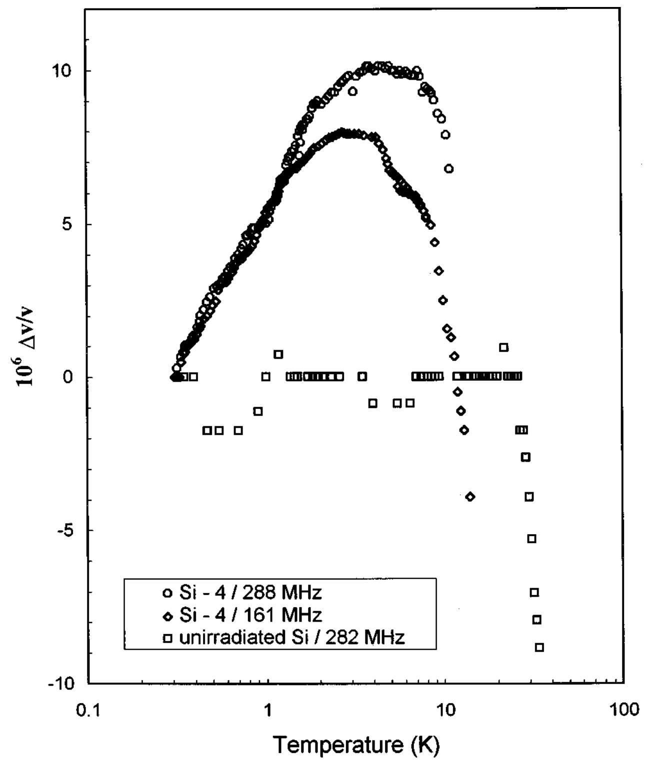

FIG. 1. Velocity change as a function of temperature for pure single-crystalline silicon at a frequency of 282 MHz and for neutron-irradiated silicon Si-4 (irradiation dose $=3.2\times10^{21}$ n/cm^2, $E>0.1$ MeV) at frequencies of 288 and 161 MHz.

Based on a pulse-interference technique,[15] measurements of changes in ultrasonic velocity were carried out for the longitudinal mode at a frequency of approximately 300 MHz and as a function of temperature (>0.3 K). Using this technique, relative velocity changes can be detected with an accuracy of the order of 10^{-7}. The conversion of an electromagnetic signal into an acoustic wave was obtained using a 30 MHz $LiNbO_3$ transducer that was attached to the sample by means of a thin layer of DC 200 Si fluid.

The influence of the irradiation on the ultrasonic velocity is shown in Fig. 1, which presents a plot of $\Delta v/v$ as a function of temperature for the pure single-crystalline silicon and the neutron-irradiated Si-4 at comparable frequencies: 282 and 288 MHz, respectively. For the unirradiated silicon a typical behavior for a pure single crystal is observed: within the experimental accuracy of the measurement, no changes in ultrasonic velocity are detected until 28 K and above 28 K a steep decrease is seen. This is in agreement with the results obtained from low-temperature ultrasonic attenuation measurements performed on the same sample, which showed a behavior that can be explained by anharmonic three-phonon interaction processes that dominate the ultrasonic and hyper-

sonic attenuation in pure crystals at low temperatures.[16]

For the irradiated silicon, a logarithmic increase with temperature is detected from 0.3 K on. At higher temperatures, the changes in the sound velocity deviate from the logarithmic law and a maximum is observed. This is similar to observations made in glasses, however, the observed changes are at least two orders of magnitude smaller than in a a-SiO_2. According to the TM the logarithmic increase corresponds to the resonant interaction between the TS and the acoustic phonons. The leveling off to a maximum can be attributed to the relaxation process which causes a decrease of the velocity with increasing temperatures.

Figure 1 also shows the results of a measurement performed on Si-4 at a frequency of 161 MHz. From this it is clear that the logarithmic increase at the lowest temperatures is frequency independent. This behavior is typical for glasses and is predicted by Eq. (1). Also conforming the predictions of the TM is the fact that for higher frequencies, the position of the maximum is located at a higher temperature.

From these results it can be concluded that the behavior of the neutron-irradiated silicon shows a remarkable similarity with the predictions of the tunneling model. Since measurements on the bulk single-crystalline starting material showed no changes in ultrasonic velocity below 28 K, the additional effect observed in neutron-irradiated silicon must be totally attributed to the neutron irradiation. Furthermore, from our Raman experiments there is evidence for a partial amorphization of the samples used. Taking into account the preliminary results we obtained from ultrasonic attenuation measurements,[17] which also showed the typical anomalies caused by TS, it can be stated that TS can be introduced in silicon by means of fast-neutron irradiation.

To obtain information on the influence of the irradiation dose on the behavior of the ultrasonic velocity and hence the amount of TS present in the material, measurements were performed on sample Si-2 which was irradiated with a dose of approximately half of that of Si-4. Figure 2 shows two measurements performed on Si-2 and Si-4 at a comparable frequency. The qualitative behavior of Si-2 is the same as that of Si-4, but for Si-2 the slope of the logarithmic increase is smaller and the position of the maximum is located at higher temperatures. The bigger slope for a higher neutron dose is consistent with an increase of the density of states of the TS with the irradiation dose.

Figure 2 also shows the best numerical fits that have been performed on the obtained data. The fits were based on the TM and were performed in a temperature range from 0.3 to 10 K. Raman processes and the effects of thermal activation were not taken into account. From these fits, the tunneling parameters C and K_3 were derived and from these $\bar{P}\gamma_l^2$ and the coupling constant γ_l were calculated. All the values for the different TM parameters are given in Table I.

As mentioned above, and confirmed by the analysis performed in the framework of the TM, the results give a clear indication for the presence of TS in the irradiated samples. From the slope of the logarithmic increase of $\Delta v/v$ below 2 K, the parameter C was derived. For an irradiation dose that is doubled, C increases, but not by a factor of 2, which is in agreement with the results of the Raman experiments. The increase of C with the dose, together with the increase of the amorphous volume fraction with the dose suggests that the

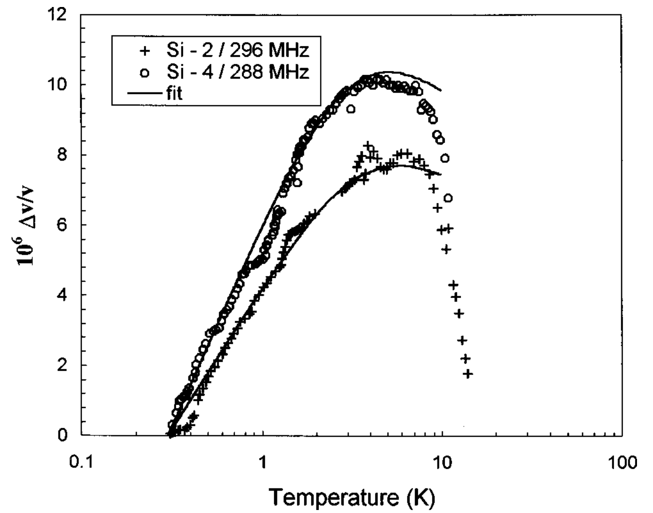

FIG. 2. Changes in ultrasonic velocity as a function of temperature for single-crystalline silicon irradiated with different irradiation doses (Si-2, dose=1.7×10^{21} n/cm^2 and Si-4, dose=3.2×10^{21} n/cm^2, $E>0.1$ MeV) at comparable frequencies.

TS's are related to the amorphous domains. Therefore the TS are most probably due to the presence of the amorphous regions and located in those regions. The value of C in neutron-irradiated silicon is of the order of 1% of the value of C for a-SiO_2, for an amorphous fraction of at least 3.7%. To obtain a similar effect in neutron-irradiated silicon and quartz, the irradiation dose has to be 10^3 times higher for silicon.[17] This means that the effect of the TS is significantly smaller in Si than in SiO_2 for similar irradiation doses. This can be explained by the fact that Si is more rigid and more difficult to amorphize than SiO_2.

The parameter K_3 is determined by the position of the maximum. Although this is more difficult to fit we did obtain—within the given accuracy—almost the same value for Si-2 and Si-4. This gives us an additional indication for the consistency of our fits.

The coupling parameter is calculated from C and K_3 using the approximation $\gamma_l^2/v_l^2=\gamma_t^2/v_t^2$, which is found for most amorphous solids.[18] It is striking that the value of the coupling parameter γ_l is distinctively higher than in a-SiO_2. This can be understood in the framework of the soft potential

TABLE I. Amorphous fraction as obtained from Raman scattering spectroscopy and TS parameters derived from ultrasonic velocity measurements performed on bulk single-crystalline silicon irradiated with fast neutrons. The accuracy for C and $\bar{P}\gamma_l^2$ is 10% and for K_3, $\bar{P}$, and γ_l is 30%.

Irradiation dose (n/cm^2), ($E>0.1$ MeV)	Si-2 1.7×10^{21}	Si-4 3.2×10^{21}
Minimal amorphous fraction (%)	3.7	4.1
Frequency (MHz)	296	288
C ($\times10^{-6}$)	3.5	5
K_3 ($\times10^7$ K^{-3} s^{-1})	16	23
$\bar{P}\gamma_l^2$ ($\times10^6$ g cm^{-1} s^{-2})	5.8	8.3
γ_l (eV)	1.83	2.18
$\bar{P}$ ($\times10^{29}$ erg^{-1} cm^{-3})	6.75	6.82

model,[19,20] which at low temperatures completely includes the TM, but which is also valid at higher temperatures. According to this model, the coupling depends on macroscopic parameters such as the longitudinal velocity, which is much higher in Si than in SiO_2, and the mean mass $\bar{M}$ of the atoms. Calculations of $\gamma_l / v_l^{5/3} \bar{M}^{5/9}$ give similar values for neutron-irradiated silicon and quartz, indicating that our results are consistent with the predictions of the soft potential model.

The density of states of the TS was also determined using the formulas of the TM. As can be seen in Table I, this value increases only very slightly with the irradiation dose. The fact that there is almost no difference in the value of $\bar{P}$ for Si-2 and Si-4 is due to the accuracy of the determination of the parameter K_3. However, from the increase in slope in the low-temperature part of $\Delta v/v$ as a function of T it is clear that by increasing the irradiation dose and thus the amount of amorphous fraction in the silicon samples, the density of the TS is increased.

Previously we performed Raman scattering experiments at room temperature in the frequency range where in amorphous solids the boson peak is seen. This peak is typical for amorphous solids and according to the soft potential model it is due to the interactions between the quasilocal harmonic oscillators. A broad band was observed at 114 cm^{-1}. Several arguments for the idea that this peak is most likely the boson peak are given in Ref. 14. Recently we also performed Raman measurements at 77 K. The data of both measurements are represented in Fig. 3. It is clear that at both temperatures this broad band is present at 114 cm^{-1}. It is found that the intensity I of this peak scales with the Bose factor. This result puts the ''glassy'' behavior of neutron-irradiated silicon clearly in evidence.

In conclusion, the results of Raman spectroscopy and measurements of the changes in ultrasonic velocity have shown that TS can be introduced in bulk fourfold-coordinated silicon by means of neutron irradiation. The density of these TS's can be controlled by changing the irradiation dose. The increase of C with the irradiation dose together with the increase of the amorphous volume fraction suggests that the TS are related to the amorphous domains. These results clearly evidence, for the first time, the fact that TS can be hosted by high coordinated bulk materials such as silicon.

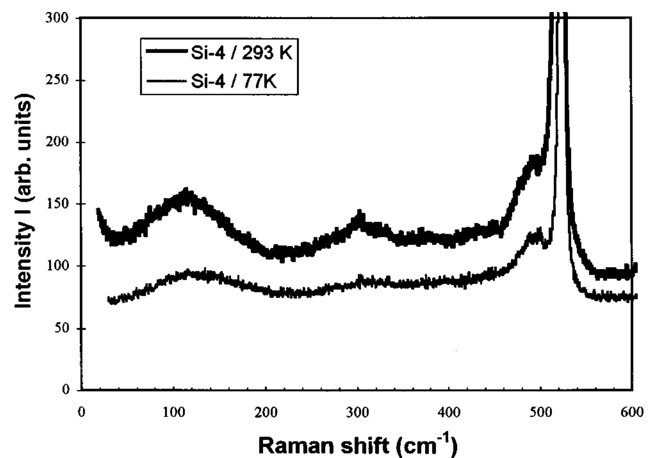

FIG. 3. Raman data as a function of the intensity I at 273 [13] and 77 K.

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