Vibrational Lifetimes of Hydrogen and Silicon MOSFET Reliability

L. C. Feldman¹, G. Lüpke², and N. H. Tolk¹

¹Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee, USA 37235 Leonard.C.Feldman@vanderbilt.edu
²Department of Applied Science, The College of William and Mary, Williamsburg, Virginia USA 23187

Abstract: We describe recent experiments which measure the vibrational lifetime of the S-H bond in various defect configurations and show the relationship between these lifetimes and silicon MOSFET reliability.

Keywords: Si-H defects, reliability
Introduction
Recently, the dynamics of hydrogen-related defects in silicon has attracted much attention [1]. Because of its small size, hydrogen (H) is easily incorporated in silicon during the growth process and can form different defects. Figure 1 shows the two-dimensional structure of hydrogen defects in silicon. The major role of hydrogen is the passivation of both shallow and deep impurity centers and other defects through the formation of complexes [2]. On the surface, H forms covalent bonds with Si dangling bonds [3]. In the bulk, H forms all kinds of interstitial, self-interstitial, vacancy-type defects or complexes with other impurities [4]. At the interface, H passivation can reduce the density of Pb centers, which is crucial in semiconductor devices [5]. These H-related defects have been well characterized [6,7].

Fig. 1. Two-dimensional model of crystalline silicon (blue dots) with various hydrogen-decorated complexes (red dots).

The addition of impurities to a host crystal, whose masses are less than the masses of the host atoms, gives rise to new vibrational modes with higher frequencies than the host crystal’s vibrational (phonon) modes [8]. The vibrational spectroscopy of these high-frequency modes has become an important probe of defects in solids and often provides information about defect structure and properties that cannot be obtained by other methods [9]. However, relatively little is known about the dynamics of local vibrational modes (LVMs) in condensed matter systems, in spite of the importance of the coupling of LVMs to the phonon bath of the host material [10,11]. Coupling between LVMs and the heat bath is responsible for the flow of energy into and out of impurity and defect complexes. This is important, because when defects act as recombination centers in semiconductors, the electronic excitation that is deposited at the defects is then available to promote defect migration and reactions, an area of defect physics that has an important impact on the degradation of electronic and optoelectronic devices. Hence a deeper
understanding of the physical properties of defects and impurities in semiconductors can be obtained by studying the dynamics of the elastic and inelastic local interactions.

Vibrational Lifetimes
Recently, we undertook a systematic study of the vibrational lifetime of various hydrogen (H) and deuterium (D) related point defects in bulk silicon and germanium [12-15]. The low-temperature lifetime of H at the bond-center site in crystalline Si and other interstitial-like complexes was found to be of the order of 10 ps, while the lifetime of vacancy-H complexes are a factor of 10 to 100 greater. The observed large disparity in measured lifetimes is unexpected based on simple theories and is as yet unexplained. These initial results indicate that local defect structure plays a crucial role in the coupling mechanism. The strong structure dependence might be explained by either pseudo-localized modes or LVMs being involved in the decay process. Being localized around these defects, such modes have much larger vibrational amplitudes on the atoms close to the Si-H bond than lattice phonons, which may cause a strongly enhanced anharmonic coupling to phonons of the Si-H stretch mode. However, significant distortions of the Si-Si bonds in the vicinity of the defects are required for pseudo-localized modes or LVMs to form, which is consistent with highly distorted interstitial-type defects having shorter lifetimes than vacancy defects. For the vacancy defects, it certainly seems plausible that the relatively large open volume of the vacancies would lead to a small interaction between the hydrogen and the surrounding silicon atoms, which would lead to a longer vibrational lifetime.

Figure 2 shows the structure of various hydrogen-decorated defects with their lifetimes. The vibrational lifetimes of $\text{H}_{BC}$, $\text{H}_2^*$, $\text{HV}$-$\text{VH}_\langle110\rangle$ are measured directly by transient bleaching technique described below. Some are estimated by their absorption line width through the equation

$$\Gamma_0 = \frac{1}{2\pi c T_1} + \frac{2}{2\pi c T_2} + \Gamma_{\text{inhom}}$$

where $\Gamma_0$ is the linewidth of absorption line, $T_1$ is the lifetime of the defect, $T_2$ is the dephasing time and $\Gamma_{\text{inhom}}$ is the inhomogeneous linewidth. The first term determines the natural linewidth of the mode, whereas the second term generally dominates the linewidth at elevated temperatures due to elastic scattering of the local mode with phonons. A good lower estimate of the vibrational lifetime can be obtained from infrared absorption spectra when the measurements are done at low temperature on a sample with a low concentration of defects and impurities.
Fig. 2. Structures of selected H-related defects in crystalline silicon. The top (bottom) row shows interstitial-type (vacancy-type) defects. The blue spheres are Si atoms and the red spheres are H atoms. The vibrational frequencies and lifetimes are also listed.

From our studies of Si-H stretch modes, we know that the vibrational dynamics of H defects is determined by anharmonic coupling with modes within the phonon bands. Two or three low-frequency modes are required to obtain qualitative agreement with the temperature dependence of the lifetimes. The nature of these exchange modes is presently not known. However, likely candidates are perturbed acoustic or optical phonons, or Si-H bend modes.

**Relationship Between the H-Si Lifetime and the Reliability of Si MOSFETS**

It is well established that the one of the last steps in the Si fabrication process is a post metallization anneal (PMA) in a hydrogen containing gas which passivates the remaining dangling bonds at the Si/SiO$_2$ interface. Unpassivated, these dangling bonds represent sufficient scattering centers to seriously degrade performance. The validity of this picture is beautifully illustrated by the work of Lyding et al [16] who substituted deuterium for hydrogen in the PMA. The
results showed that both hydrogen and deuterium had the same effect in terms of passivation, as expected, but that the rate of device performance degradation was unexpectedly reduced with deuterium passivation. In general, the degradation effect is understood as the electron impact induced desorption of hydrogen (deuterium), thus exposing the scattering centers. This “giant isotope effect” was in agreement with earlier results of Shen at al \[17\] and Foley et al \[18\] who showed that the probability of desorption of deuterium on clean silicon surfaces was significantly smaller than for hydrogen desorption. Based on well-understood surface science experiments the bond strength of both Si-H and Si-D is \(~3eV\). The explanation for these isotope effects then requires an understanding of how low energy electrons (\(<3eV\)) can induce desorption of hydrogen and why deuterium desorption rates are smaller than hydrogen desorption rates. This was explained most simply by Persson et al \[19\] in their truncated harmonic oscillator model (sometimes referred to as the thermal heating model). In this picture there is a competition between excitation to higher levels of the oscillator and the decay to lower levels. With a sufficiently high excitation rate, compared to the decay rate, it is possible to work up the energy levels. If a sufficiently high level is achieved desorption may occur. For example in the hydrogen-silicon system the first harmonic level corresponds to \(~0.25eV\) excitation energy. Thus excitation to the 12th level is required to reach the 3eV value of the binding energy.

Using this model Persson et al derived a general expression for the dissociation rate, \(R\), associated with excitation to the \(n\)th channel as

\[
R \sim \frac{n+1}{T_1} \left[ \frac{\Gamma_{\text{exc}}}{\Gamma_{\text{exc}} + T_1} \right]^{n+1},
\]

(2)

where \(\Gamma_{\text{exc}}\) is the excitation rate, due to electron collisions, and \(T_1\) is the decay rate, similar to the lifetime measurements described above. Unfortunately it is not possible to measure the actual lifetime of passivating hydrogen in a genuine MOSFET structure. There is insufficient hydrogen for such an experiment. However we can attempt to evaluate equation (2), using estimates of the excitation rate and the measured lifetime in a configuration as close to the dangling bond as possible.

For the lifetime we use the value of 296 psec for the H-V-V-H center shown in Fig 2. Alternatively we might use the value of \(~800\)psec measured by Guyot-Sionnest et al \[20\] for the bare surface. In any case the decay rate is clearly in this range.

For the excitation probability we resort to atomic physics concepts. The excitation probability is given as

\[
\Gamma_{\text{exc}} = \sigma \cdot j
\]

(3)
where $s$, corresponds to the cross section for ~0.25 eV excitation by a low energy electron and $j$ is the lateral current density in the MOSFET. The current density in a typical MOSFET is estimated as $6 \times 10^{26}$ electrons/cm$^2$/sec, corresponding to a MOSFET current of 1mA and an effective area of (1 micron)x(10 Angstroms). The atomic physics literature [21] indicates that the cross-section for excitation is ~$10^{-16}$/cm$^2$, so that $\Gamma_{exc} = 6 \times 10^9$/sec where we have assumed that all electrons within the channel are available for excitation. Thus the excitation rates and the decay rates are comparable and multiple excitation through the harmonic levels is indeed possible. Using a standard MOSFET configuration Chen et al [22] confirmed this general picture by showing that the degradation rate is dependent on the current and not the integrated charge.

It is interesting to note that $R$ is always less than 1. For deuterium desorption one must reach the 17th level since the harmonic-like energy level is reduced by $\sqrt{2}$ and the binding energy of 3eV remains the same as for hydrogen. Then it is clear that since $R < 1$ the desorption rate for deuterium is significantly less than for hydrogen, even accounting for some increase in the excitation cross-section.

**Conclusion**

In summary, we have studied the lifetimes of a selection of Si-H stretch modes of point defects in Si. The lifetimes of interstitial-type defects were found to be very short (1.6-8 ps), whereas vacancy-type defects have lifetimes up to several hundreds of picoseconds – two orders of magnitude variation. The strong dependence of the lifetime on the atomic structure of the defects suggests that pseudo-localized modes or LVMs are involved in the vibrational relaxation of Si-H bonds of point defects in solids. We have also discussed how these lifetime measurements give an indication of the fundamental parameters controlling Si MOSFET reliability values.

**Acknowledgments**

The authors thank Michael Budde (Aarhus University, Denmark) for his pioneering efforts in the lifetime measurements and for many fruitful discussions. We gratefully acknowledge the staff at the TJNAF FEL and W. M. Augustyniak for technical assistance, and M. J. Kelley for providing his FTIR spectrometer. This work was supported in part by DOE through Grant No. DE-FG02-99ER45781 (C.W.M and V.U.), ONR (C.W.M and V.U.), NSF through Grant No. DMR-00-76027 (C.W.M), and Tomas F. and Kate Miller Jeffress Memorial Trust through Grant No. J-545 (C.W.M).

**References**


DOI References

doi:10.1103/RevModPhys.50.607

doi:10.1103/PhysRevLett.87.145501

doi:10.1103/PhysRevLett.80.1336

doi:10.1103/PhysRevLett.64.2156

doi:10.1063/1.1516863

doi:10.1126/science.268.5217.1590

doi:10.1103/PhysRevLett.80.1336