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Deep-level defects in silicon and the band-edge hydrostatic deformation potentials

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Evidence for an energy reference level based on substitutional transition-metal defect levels in semiconductors is presented and used to obtain the values for the band-edge hydrostatic deformation potentials in silicon. From the pressure derivatives of Pt and Pd acceptors in silicon we derive values of $\Xi_d = -0.5$ eV and $a_v = +0.9$ eV. These values are consistent with recent theoretical calculations and with the analysis of acoustic-phonon-limited electron and hole mobility.

The application of stress or pressure to semiconductors containing point defects has long been a valuable probe of defect structure. In particular, the pressure derivatives of defect energy levels have been used as a means to distinguish between defects which are dominated by extended Coulombic potentials (effective-mass-like levels) and defects which are dominated by strong local potentials (deep levels).[1] Such experiments have shown that the effective-mass defect levels are pinned to the nearest band edge, while the deep-level defect levels are not. These results are a consequence of the relation between defect-potential localization and the extent of k space required to adequately describe the defect wave function. At this level of understanding, experiments and theory have been able to quantify defect stress properties only with respect to the semiconductor band edges. The band edges shift with pressure, however, and therefore cannot be used as a reference in absolute terms. There are several reasons why an absolute reference energy would be desirable. First, relating the deep-level pressure derivatives to the band edges does not provide particularly useful insight into the deep-level structure because deep-level defect properties are dependent on the general features of the semiconductor band structure and not the nearest band extremum. Second, the shifts of the band edges under pressure contribute to acoustic deformation potential scattering of electrons and holes and it would be of fundamental interest to be able to measure these band-edge deformation potentials directly. Accurate knowledge of the band-edge deformation potential is also crucial for measurements of volume relaxation around a defect.[2] Finally, by knowing how the total energy of a defect changes with a changing lattice constant one can determine the strength of the defect-lattice coupling, which has importance for the phenomena of multiphonon recombination and lattice relaxation. In this article, we present evidence for a transition-metal-based reference level in silicon from which pressure-induced changes in both the band structure and deep-level defects can be measured.

The discovery of a reference energy in semiconductors arose in the context of band-edge offsets at heterojunction interfaces. Several investigators defined an energy level called the charge neutrality level[3,4] or dielectric mean energy[5] which is forced to line up across a semiconductor heterointerface under the requirement of minimum surface polarization. This neutrality level can be roughly identified with the average sp^3 hybrid energy, or equivalently with the center of gravity of Jone's zone (or dielectric) gap. The electronic structure of some deep-level defects is strongly determined by this dominant feature of the band structure, and consequently these deep levels are closely tied to the neutrality level. This appears to be the case for substitutional transition-metal impurities.[6-8] It has been proposed that transition-metal defect levels in III-V semiconductors are locked within an additive constant to the neutrality level[9] and therefore act as reference levels from which changes in band structure can be measured. We recently extended this principle to include the effect of stress on band structure and provided experimental evidence of this principle as well as values for the band-edge deformation potentials[10] in GaAs and InP. The values for these deformation potentials result from hydrostatic pressure experiments performed on transition-metal defects among several different charge states. By measuring the pressure derivative of the transition-metal defect levels one is in fact measuring the pressure derivative of the band edge. The purpose of this paper is to extend this result from the III-V compounds to silicon, using published pressure derivative data.

The transition-metal reference level translates naturally from the III-V compounds to silicon. In practice, however, the application to silicon is complicated by several difficulties experienced in silicon, but not in most of the III-V compounds. First, most transition-metal impurities in silicon occupy interstitial sites and do not qualify as suitable reference levels, as will be shown later. The transition metals that do assume substitutional sites are heavy elements with $4d$ or $4f$ electrons in the core, and it is not clear *a priori* how these inner core electrons influence the electronic structure of these defects. The second difficulty arises from the fact that the pressure derivative of the indirect band gap in silicon is an order of magnitude smaller than the pressure derivatives of the direct gaps in most of the III-V semiconductors. While this should present no fundamental difficulties to the theory, the ability to compare theoretical calculations of band-edge deformation potentials to experimental values is hampered by the present accuracy of the calculations. Despite these difficulties, we feel that sufficient experimental and theoretical evidence exists to define an absolute reference level in silicon from which defect as well as band properties can be measured.

Deep-level defects which are candidates for defining a reference level should share a common pressure derivative that is independent of charge state, chemical species and binding energy. We established this fact experimentally for the substutional transition-metal impurities in GaAs and showed that the corresponding band-edge deformation potentials were consistent with mobility experiments and with theoretical calculations. The analogous system in Si are the substitutional transition elements Pd and Pt. The pressure derivatives of these isolated elements, as well as several complexes, have been measured previously.[11] The acceptor level of both impurities [Pd(−/0) and Pt(−/0)] have equal pressure derivatives, which are similar to the pressure derivative of the Au acceptor level.[2,12] On the other hand, the pressure derivatives of the levels assigned as Pt(0/+) and Au(0/+) have substantially different values. At first sight, this would cast doubt on the validity of using these heavy transition-metal elements as reference levels. However, additional defect pressure derivatives are available which can explain the discrepancy. Taking the value of the pressure derivative of Pd(−/0) and Pt(−/0) as the origin, the pressure derivtives of many deep-level defects in Si are plotted in Fig. 1 along with the pressure derivatives of the band edges. The defect values fall into three general classes: (1) shallow levels with pressure derivatives pinned to the nearest band edge; (2) interstitial transition metals with large negative pressure derivatives depending on the chemical species; and (3) deep substitutional impurities including transition metals and deep double donors which all have similar pressure derivatives. This third class of defects satisfies the criterion for providing an absolute reference level. The Pt level at Ev+320 meV, which had previously been assigned as the substitutional Pt(0/+) donor, has a pressure derivative consistent with the interstitial transition metals. Considering the propensity of the transition metals in Si to occur interstitially, this Pt level is likely to arise from the interstitial configuration and therefore explains the discrepancy between the pressure derivtives of the two Pt levels. Pressure derivatives of transition-metals defects in silicon should therefore provide a criterion for distinguishing substitutional from interstitial impurities (or complexes).

The inclusion of the chalcogenides Se and S in the class of substitutional impurities which define a reference level has not previously been suggested. Their structure would seem to be substantially different from the structure of substitutional transition metals which locks the transition metals to the neutrality level. In fact, the levels arising from Te do not have pressure derivatives similar to those of Se and S. However, the chemical trend in the pressure derivatives of the chalcogenides shows a remarkable feature: The pressure derivatives for decreasing Z approach the value defined by the Pd and Pt levels. Such behavior may be reconcilable with theories of substitutional deep traps in covalent semiconductors[14] which do predict asymptotic behavior for strongly electronegative substitutional elements. These defects take on vacancylike wave functions, as do the substitutional transition metals which are locked to the neutrality level. Therefore, the near equality of the low-Z chalcogenide pressure derivative with the pressure derivative of substitutional Pd and Pt provides additional experimental evidence for the existence of a reference level in Si.

The deformation potentials of the band edges, measured with respect to the Pd an Pt levels, are $a_c = \Xi_d + \frac{1}{3}\Xi_u = +2.4$ eV and $a_v = +0.9$ eV. From the reported value[15] of $\Xi_u = 8.6$ eV, we determine $\Xi_d = -0.5$ eV.

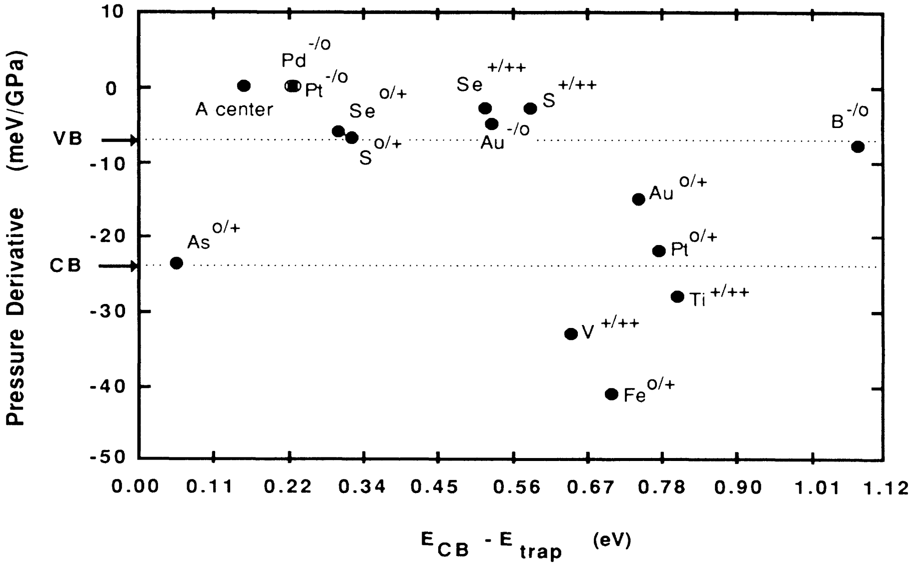

FIG. 1. Pressure derivatives of several defects in Si. The origin is taken as the value of the pressure derivative of the Pd(−/0) and Pt(−/0) levels. The pressure derivatives of the band edges are also included. The data fall under three broad categories: shallow defects pinned to the band edges; substitutional defects with pressure derivatives locked to the reference level; and interstitial transition-metal defects. Data are from Refs. 1, 2, 11, and 13.

These values can now be compared to theoretical calculations and mobility experiments to check for consistency. The most accurate calculation of the band-edge deformation potentials in Si comes from *ab initio,* self-consistent pseudopotential calculations[16] of the valence band which yield a value $a_v = +0.8$ eV. The conduction-band deformation potential is obtained by adding the deformation potential of the band gap to this value. This gives $a_c = +2.3$ eV. This excellent agreement between our values and the calculated values is a further indication that the pressure derivatives of the substitutional transition metals in Si provide an accurate reference level, although such close agreement between experiment and theory is somewhat fortuitous since the error on the calculation is estimated to be ± 1 eV.

A more important test of our values for the band-edge deformation potentials comes from mobility measurements. Acoustic-phonon-limited mobility is given by[17]

$$\mu = \tfrac{1}{3} e(\tau_{\parallel}/m_{\parallel}^{*} + 2\tau_{\perp}/m_{\perp}^{*}) \ , \tag{1}$$

where

$$\tau_{\perp} = \tau_0 T^{-3/2}(E/k_B T)^{-1/2} \tag{2}$$

and

$$\tau_0 = \frac{2\sqrt{2}\pi \hbar^4 c_1}{3(m_{\perp}^{*2} m_{\parallel}^{*})^{1/2} k_B^{3/2} \Xi_u^2 [1.33(\Xi_d/\Xi_u)^2 + 1.15(\Xi_d/\Xi_u) + 1.18]} \ , \tag{3}$$

where c_1 is the longitudinal elastic constant and E is the electron energy. It has been found[18] that a best fit to experimental data on electron mobility in silicon is obtained for $\tau_0 = 3.56 \times 10^{-9}$ sec K$^{3/2}$. Using Eq. (3) with our empirical condition $\Xi_d + \frac{1}{3}\Xi_u = 2.4$ eV we find $\Xi_u = 9$ eV and $\Xi_d = -0.6$ eV. This value of Ξ_u compares very favorably with the reported value of 8.6 eV from the effects of uniaxial stress on indirect excitons.[15] Therefore our determination of Ξ_d using the transition-metal pressure derivatives is consistent with the electron mobility data, and is certainly more accurate than previous values obtained from mobility data alone.

The effective deformation potential describing scattering of holes by acoustic phonons is

$$\Xi_{\text{eff}} = a_v^2 + (c_1/c_t)[b_v^2 + d_v^2/2] \ , \tag{4}$$

where c_t is the transverse elastic constant. The deformation potentials $b_v = -2.2$ eV and $d_v = -5.1$ eV are well established.[19] Using our value of $a_v = +0.9$ eV we obtain $\Xi_{\text{eff}} = 7.3$ eV which again is very close to the value of 7.5 eV found from hole mobility analysis in *p*-type silicon.[20] Therefore, we have found that the values of the hydrostatic band-edge deformation potentials in silicon determined from substitutional transition-metal presure derivatives provides a basis for a consistent explanation of electron and hole mobilities. In conclusion, we have established strong evidence for a pressure reference level in silicon based on heavy substitutional transition metals as well as on low-*Z* chalcogenides. From this reference level we provide the first accurate value for Ξ_d which is consistent with the best mobility data.

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