

Hole effective masses in relaxed $\text{Si}_{1-x}\text{C}_x$ and $\text{Si}_{1-y}\text{Ge}_y$ alloys

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(Received 11 November 1996; accepted for publication 11 January 1997)

We report hole effective mass calculations of $\text{Si}_{1-x}\text{C}_x$ and $\text{Si}_{1-y}\text{Ge}_y$ alloys. All calculations are based on a 16×16 Hamiltonian matrix constructed from the linear combination of atomic orbital approximation with spin-orbit interaction taken into consideration. The 1 meV constant energy surfaces below the valence band edge are used to determine the nominal hole effective masses. The effective masses of light hole and heavy hole of $\text{Si}_{1-y}\text{Ge}_y$ alloys vary as linear functions of Ge content and increase linearly as the hole energy increases from 1 to 15 meV. The heavy hole effective masses of $\text{Si}_{1-x}\text{C}_x$ alloys, however, exhibit a totally different trend. The effective mass of $\text{Si}_{1-x}\text{C}_x$ remains relatively unchanged from $x=0.0$ to $x=0.9$, and increases abruptly by a factor of two from $x=0.9$ to $x=1.0$. The nonparabolicity increases as the C content rises up to $x=0.9$, and nearly disappears when turning into pure diamond. The interaction between the split-off hole band and the heavy hole band is proposed for the anomalous behavior of the heavy hole effective masses of SiC alloys. © 1997 American Institute of Physics. [S0003-6951(97)02911-2]

The strained SiGe on Si substrates has made tremendous progress in high speed electronic applications with heterojunction bipolar transistor (HBT) performance of f_T (cutoff frequency) and f_{\max} (maximum frequency of oscillation) of 117¹ and 160 GHz,² respectively, having been reported. However, the device performance is limited by the small critical thickness of these strained layers. Over the past few years, it has been shown that the incorporation of carbon can reduce the strain in these layers,³ high quality SiGeC materials with defect-free photoluminescence can be epitaxially grown,⁴ and the Si/SiGeC/Si heterojunction bipolar transistors can be successfully fabricated.⁵ For theoretical work, most studies⁶⁻⁸ are focused on band gap issues of the SiGeC alloys. Some unusual behaviors of C incorporation have been predicted or demonstrated. For example, the $\text{Si}_{1-x}\text{C}_x$ alloy becomes metallic when $x=0.125$ ⁷ and the small C content can reduce the band gap of relaxed SiGeC alloys,⁹ despite the wide band gap of diamond (5.5 eV). However, little experimental and theoretical work on valence band structures of these alloys has been reported. We, therefore, performed theoretical prediction of hole effective masses in bulk alloys and reported an anomalous effect on hole effective masses due to the carbon incorporation into silicon.

Calculations are based on the framework of linear combination of atomic orbitals (LCAO) with spin-orbit interaction taken into consideration. The Hamiltonian operator is given by

$$H = \frac{p^2}{2m_0} + \sum_j V(\mathbf{r}-\mathbf{R}_j) + \sum_j \xi(\mathbf{r}-\mathbf{R}_j) \mathbf{L}_j \cdot \mathbf{S}_j,$$

where m_0 gives the free electron mass, \mathbf{R}_j indicates the location of the atoms, and the $\mathbf{L}_j \cdot \mathbf{S}_j$ is spin-orbit interaction term with coupling strength ξ .

The Hamiltonian matrix is constructed by the eight $s-p$ hybridization orbitals in the diamond lattice with direct prod-

uct of spin wave functions to form a 16×16 matrix. The spin independent matrix elements for Si and Ge are adopted from Ref. 10 and that of C is from Ref. 11, where only nearest neighbor interaction is considered. The spin dependent matrix elements¹² are determined such that the resulting spin-orbit splittings ΔE_{s-o} (split-off energy) of the valence band are 0.044, 0.0, and 0.29 eV for pure Si, C, and Ge, respectively.¹³ There is no free parameter left in the calculations. With virtual crystal approximation (VCA), all values of the parameters involved in the matrix elements used for the alloy $A_{1-x}B_x$ are obtained from the linear interpolation of constituent semiconductors. In all the cases, warped constant-energy surfaces for valence bands are found in our calculations (Fig. 1), similar to those obtained from the $\mathbf{k} \cdot \mathbf{p}$ method. We fit constant energy surface of valence band

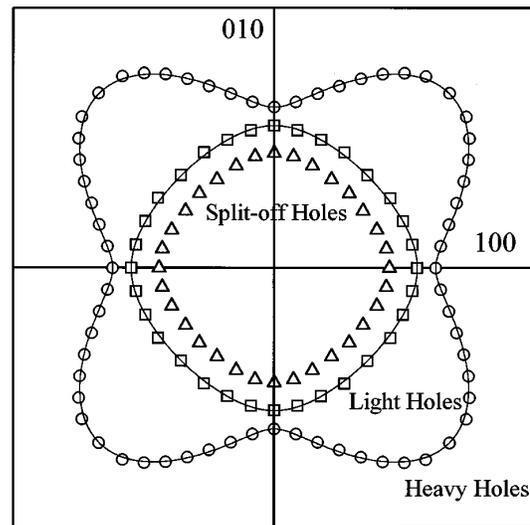


FIG. 1. Warped constant-energy contours, for example, in $\text{Si}_{0.9}\text{C}_{0.1}$ at energy 0.1 eV. The solid lines are plotted using $E_{\mathbf{k}} = -\hbar^2/2m_0 \{A k^2 \pm [B^2 k^4 + C^2(k_1^2 k_2^2 + k_2^2 k_3^2 + k_3^2 k_1^2)]^{1/2}\}$. The $-$ sign is used for heavy holes with $A=3.58$, $B=0.547$, and $C=4.45$ and the $+$ sign is for the light holes with $A=3.08$, $B=0.787$, and $C=2.53$.

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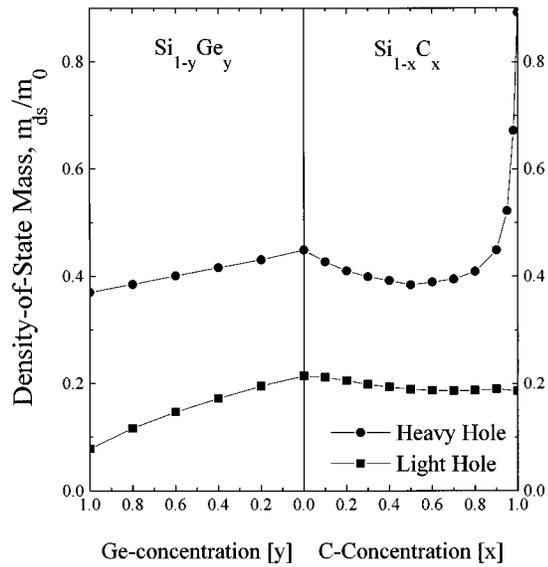


FIG. 2. Heavy hole and light hole effective masses of $\text{Si}_{1-x}\text{C}_x$ and $\text{Si}_{1-y}\text{Ge}_y$ alloys.

structure with $E_{\mathbf{k}} = -\hbar^2/2m_0\{Ak^2 \pm [B^2k^4 + C^2(k_1^2k_2^2 + k_2^2k_3^2 + k_3^2k_1^2)]^{1/2}\}$,¹⁴ where the $-$ sign and $+$ sign refer to the heavy hole and light hole bands, respectively. In the units of m_0 , the density-of-state effective masses of heavy and light holes (m_{hh} and m_{lh}) are calculated exactly from the integral $[1/4\pi \int \sin \theta d\theta \int d\phi Q_{\pm}^{-3/2}]^{2/3}$, where $Q_{\pm} = A \pm \sqrt{B^2 + C^2(\sin^4 \theta \cos^2 \phi \sin^2 \phi + \sin^2 \theta \cos^2 \theta)}$ through averaging over the directionally dependent effective masses,¹⁴ instead of using the approximate value $[A \pm \sqrt{B^2 + C^2/6}]^{-1}$.¹⁵ To obtain the best fit of constant energy surfaces, two different sets of A, B, C parameters are used for the heavy hole and light hole bands, while only one set of parameters is used for both heavy hole and light hole bands in the $\mathbf{k} \cdot \mathbf{p}$ method. The energy-dependent effective mass is

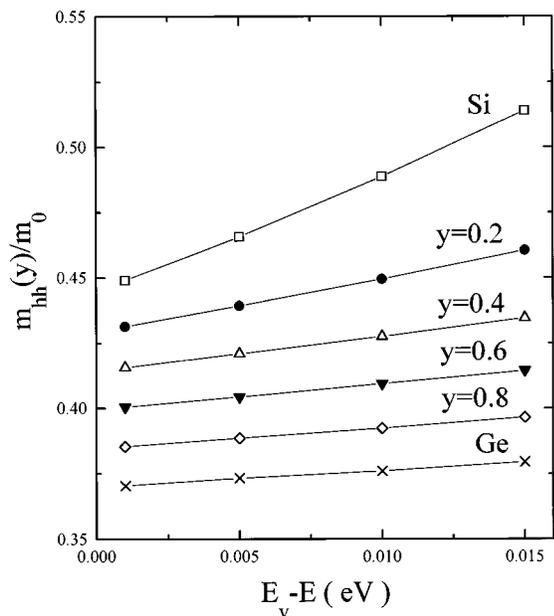


FIG. 3. Energy dependence of the heavy hole effective masses of $\text{Si}_{1-y}\text{Ge}_y$ alloys.

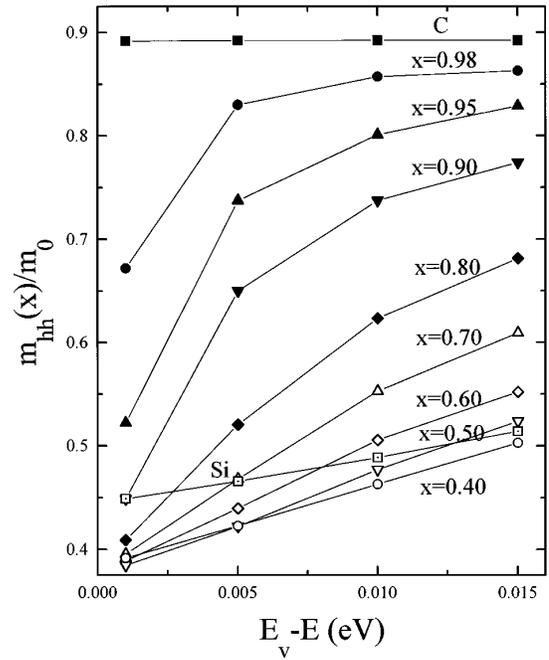


FIG. 4. Energy dependence of the heavy hole effective masses of $\text{Si}_{1-x}\text{C}_x$ alloys.

also obtained by using different energy contours. To compare the effective mass of different alloy composition, the nominal value of effective mass is determined at 1 meV below the valence band edge.

For $\text{Si}_{1-y}\text{Ge}_y$ alloys, both heavy and light hole effective masses decrease linearly as Ge content increases (Fig. 2). The linear dependency agrees qualitatively with the experimental results for $y < 0.5$.¹⁶ To study the nonparabolicity of the valence band structure, the heavy hole effective mass is plotted as a function of hole energy (Fig. 3). The effective masses of both heavy hole and light hole increase linearly with the increasing hole energy and can be expressed as $m(E) = m(0)(1 + \alpha E)$, α being nonparabolicity parameter, similar to the direct band gap materials.¹⁷ The α value of heavy hole band is 10.2/eV for pure Si, and monotonically decreases to 1.77/eV for pure Ge (Fig. 5). The α values for light hole bands are roughly constants around 1.32/eV for all the $\text{Si}_{1-y}\text{Ge}_y$ alloys.

Our calculations of heavy hole effective masses for $\text{Si}_{1-x}\text{C}_x$ alloys, however, show a totally different trend as the carbon concentration increases (Fig. 2). Although Si has a smaller heavy hole effective mass than C ($m_{\text{hh,Si}} = 0.45m_0$ and $m_{\text{hh,C}} = 0.89m_0$), m_{hh} decreases slightly as the carbon concentration increases up to about 50% and does not make even with that of silicon until about 90% of carbon concentration. In other words, starting from the carbon rich side, the effect of silicon incorporation is dramatic. It shows that with 2% of silicon incorporation into carbon, there is about a 50% drop of m_{hh} in-between the pure carbon and pure silicon. The calculated heavy hole effective mass of pure C is $0.89 m_0$, similar to the previously reported value of $1.1 m_0$, while some other lower values (0.6, $0.4 m_0$) were also reported.¹⁸ The calculated value of Si heavy hole effective mass is $0.45 m_0$, very close to the tabulated value of $0.49 m_0$.¹⁹ For

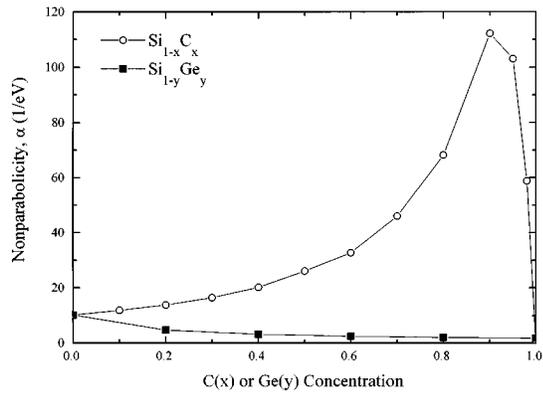


FIG. 5. Nonparabolicity parameter α values of $\text{Si}_{1-x}\text{C}_x$ and $\text{Si}_{1-y}\text{Ge}_y$ alloys.

$x < 0.5$, the nonparabolicity in $\text{Si}_{1-x}\text{C}_x$ is stronger than that in the $\text{Si}_{1-y}\text{Ge}_y$, but still can be represented by a linear function of energy (Fig. 4), and the α values are obtained accordingly (Fig. 5). In the range of $0.6 \leq x \leq 1.0$, the energy dependence of hole effective masses becomes nonlinear. The corresponding α values are calculated using m_{hh} values at 1 and 5 meV below the valence band edge. A monotonic increase of the nonparabolicity parameter to 112.2/eV is found up to 90% C incorporated into Si (Fig. 5), but the α value soon drops to 0.088/eV as the alloy turns into pure C. Note that in the region of $0.9 \leq x \leq 1.0$, the heavy hole effective mass also increases rapidly as the C concentration increases. The composition dependence of light hole effective mass of $\text{Si}_{1-x}\text{C}_x$ has a similar trend, but this effect is not as significant due to the similar light hole effective masses of silicon and diamond ($\sim 0.2 m_0$). The α values of light hole bands drop rather monotonically from 1.52/eV of pure Si to 0.117/eV for pure C.

The origin of this anomalous effect can be understood by the interaction between the heavy hole band and the split-off hole band. In our calculation, the spin-orbital coupling strength ξ was obtained to have the split-off energies of 0.044 and 0.0 for Si and C, respectively, and was linearly interpolated for SiC alloys. As a result, the ΔE_{s-o} of SiC alloys is also a linear function of C content. The incorporation of silicon into carbon, on top of changes of other parameters, such as lattice constant and overlap integrals, etc., in the VCA scheme, is equivalent to gradually turning on the spin-orbit interaction which removes the original double degeneracy between heavy hole and split-off hole bands. At small Si concentration in the C, the split-off hole band is very close to the heavy hole band and the interactions between the two band edges are relatively stronger compared to the Si rich case where two band edges are rather far apart. For example, split-off energy of the $\text{Si}_{0.02}\text{C}_{0.98}$ is about 0.9 meV, very close the hole energy of 1 meV where the nominal effective mass is evaluated. This causes a strong defor-

mation of the heavy hole band near the band edge of $\text{Si}_{0.02}\text{C}_{0.98}$ and thus the nominal effective mass deviates from linear behavior dramatically. The analysis also explains the expected linear dependence of $m_{\text{hh}}(\text{Si}_{1-y}\text{Ge}_y)$ on the Ge concentration. With ΔE_{s-o} for pure Ge equal to 0.29 eV, the incorporation of Ge into Si has an effect of broadening the ΔE_{s-o} , which is already 0.044 eV. Therefore, the interactions of the heavy hole band and the split-off hole band edges would be roughly the same on the edge of valence band as the Ge concentration increases and thus results in a linear behavior of $m_{\text{hh}}(\text{Si}_{1-y}\text{Ge}_y)$. This accounts for the result that nonlinear energy dependence of m_{hh} for $\text{Si}_{1-x}\text{C}_x$, is in the range of $0.6 \leq x \leq 1.0$, where split-off energy is within 17 meV, comparable with the range of calculated effective mass (1–15 meV).

By comparing the behaviors of m_{hh} as Ge and C are incorporated into Si, we conjecture that the variation of the heavy hole effective mass in terms of mixing concentrations would be smooth if both the constituent semiconductors of the alloys are with large spin-orbit splittings, while the anomalous behavior would be found if the spin-orbit splitting of any one of the constituents is small.

This work is supported by the National Science Council of the Republic of China under Contract Nos. NSC86-2112-M-005-013 (C. Y. Lin) and NSC86-2215-E-002-0041 (C. W. Liu).

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