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Materials Chemistry and Physics 52 (1998) 31–35

MATERIALS CHEMISTRY AND PHYSICS

# Valence band properties of relaxed $Ge_{1-x}C_x$ alloys

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Received 19 December 1996; received in revised form 21 January 1997; accepted 3 June 1997

**Abstract**

We report hole effective mass calculations of $Ge_{1-x}C_x$ alloys. A $16\times16$ Hamiltonian matrix constructed from the linear combination of atomic orbitals with spin-orbit interaction terms is used for the calculations. The properties of alloys are calculated under the virtual crystal approximation. The 1 meV constant energy surface below the valence band edge is used to determine the nominal hole effective masses. Calculations are carried out by taking the diamond split-off energy $\Delta E_{s-o}(C)$ as 0 and 6 meV, respectively. In both cases, the light hole band results of $Ge_{1-x}C_x$ alloys agree to within less than 1%. The effective masses of light hole increase monotonically from 0.078 $m_0$ (for pure Ge) to 0.19 $m_0$ (for pure C) while the non-parabolicity drops rather monotonically. The heavy hole effective masses of the alloys show a highly non-linear dependence on the carbon content ($x$). The results in both cases are indistinguishable from $x=0.0$ to about $x=0.9$; it decreases slightly from $x=0.0$ to $x=0.5$ and increases slowly from $x=0.5$ to $x=0.9$. The values increase for $x>0.9$. With $\Delta E_{s-o}(C)=0$ meV, there is an abrupt increase by a factor of two from $x=0.97$ to $x=1.0$ to a value of 0.89 $m_0$. For $\Delta E_{s-o}(C)=6$ meV, a similar trend is found with a lower value of 0.45 $m_0$ at $x=1.0$. The non-parabolicity of the heavy hole masses increases monotonically from $x=0.0$ to $x=0.99$, and nearly disappears for pure diamond for $\Delta E_{s-o}(C)=0$ meV, while a monotonic increase of non-parabolicity is found for $\Delta E_{s-o}(C)=6$ meV from pure Ge to pure C. 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 GeC alloys. 

*Keywords:* GeC alloys; Hole effective mass; Linear combination of atomic orbitals; Valence band; Non-parabolicity

## 1. Introduction

Recently, alloys based on group IV elements (C, Si, Ge, and Sn) have attracted great attention for the heterojunction applications of Si-based electronic and optoelectronic devices. Bipolar transistors [1,2] and field effect devices [3,4] using SiGe technologies have been demonstrated with greatly improved performance as compared with conventional Si devices. To overcome the critical thickness limit, the emerging SiGeC technology is utilized to expand the applications of SiGe technologies, where the thick layer is required such as pin photo-detectors [5] as well as other novel applications. The substitutional carbon in SiGeC alloys can compensate the compressive strain of SiGe alloys grown on Si. For the extreme case, the GeC can also serve the bandgap engineering applications on Si substrates without the possible formation of silicon carbide precipitate in the SiGeC alloys [6]. Since the solubility of C in Ge is about $10^8$ cm$^{-3}$ in thermodynamic equilibrium [7], the GeC alloy is very difficult to prepare and little of its properties is known. Until very recently, the metastable growth of single crystalline GeC has been demonstrated by molecular beam epitaxy [8] and chemical vapor deposition [9] with renewable interest. The experimental work of GeC is mainly focused on growth and structural properties. For the theoretical work, the bandgap of relaxed GeC alloys has been predicted by virtual crystal approximation [10]. However, very limited electronic properties of GeC have been studied. Therefore, we performed the first theoretical study of valence band properties of bulk GeC alloys and reported an anomalous effect on hole effective masses due to the carbon incorporation into Ge.

## 2. Method

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

$$H=\frac{p^2}{2m_0}+\sum_j V(r-R_j)+\sum_j \xi(r-R_j)L_j\cdot S_j, \qquad (1)$$

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0254-0584/98/$19.00 
*PII* S0254-0584(97)02001-4

where $m_0$ gives the free electron mass, $R_j$ indicates the location of the atoms, and the $L_j \cdot S_j$ is spin-orbit interaction term with coupling strength $\xi$, given by

$$\xi(r) = \frac{1}{2m_0^2c^2r}\frac{dV}{dr} \tag{2}$$

where $V$ is Coulomb interaction potential. The Hamiltonian operator is represented in a basis composed of sixteen Bloch sums obtained from the eight $s$–$p$ hybridization orbitals in the diamond lattice with direct product of spin wave functions. A $16 \times 16$ Hamiltonian matrix is constructed by considering only the nearest neighbor interaction. The values of spin independent matrix elements for Ge are adopted from Ref. [11] and that of C is from Ref. [12]. The spin dependent matrix elements [13] are determined such that the resultant spin-orbit splittings $\Delta E_{s-o}$ (split-off energy) of the valence band are matched with the reported values: 0 meV [14] and 6 meV [15] for pure C and 290 meV for pure Ge [14], respectively. No free parameters are left in our calculations. The electronic energy band structure is studied through numerical diagonalization of the Hamiltonian matrix. For $Ge_{1-x}C_x$ alloys, all values of the parameters $P$ involved in the matrix elements are determined under virtual crystal approximation (VCA) through linear interpolation of constituent semiconductors, i.e. $P_{Ge_{1-x}C_x} = (1-x)P_{Ge} + xP_C$. Similar to those obtained from the $\mathbf{k} \cdot \mathbf{p}$ method which is accurate near the Brillouin zone center, warped constant-energy surfaces are found in all the alloys from using the constructed LCAO Hamiltonian matrix (Fig. 1). We fit constant energy surface of valence band structure with

$$E_k = \frac{-\hbar^2}{2m_0}[Ak^2 \pm \sqrt{B^2k^4 + C^2(k_1^2k_2^2 + k_2^2k_3^2 + k_3^2k_1^2)}] \tag{3}$$

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 $m_{lh}$) through averaging over the directionally dependent effective masses are calculated exactly from the integral

$$\left[\frac{1}{4\pi}\int\int \sin\theta d\theta d\phi Q_{\pm}^{-3/2}\right]^{2/3} \tag{4}$$

where $Q_{\pm} = A \pm \sqrt{B^2 + C^2(\sin^4\theta\cos^2\phi\sin^2\phi + \sin^2\theta\cos^2\theta)}$ [16] ($-$ for heavy hole and $+$ for light hole). To obtain the best-fit of constant energy surfaces, two different sets of $A$, $B$, and $C$ 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. Constant-energy contours at different energies $E_k$ are used to obtain the energy dependence of hole effective masses. 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.

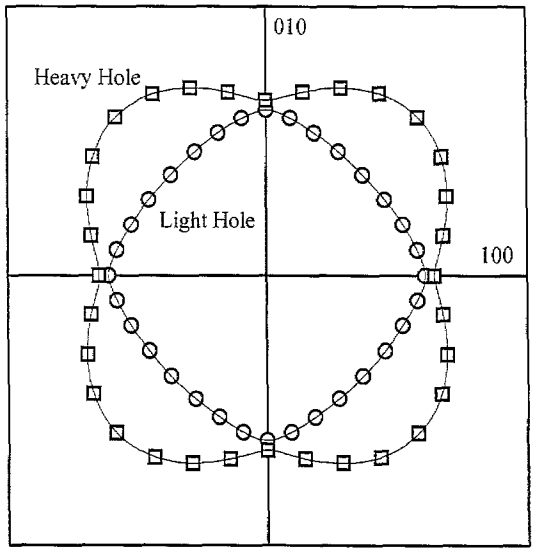


Fig. 1. Warped constant-energy contours, for example, in $Ge_{0.8}C_{0.2}$ at energy 1 meV below the valence band edge with $\Delta E_{s-o}(C) = 0$. The solid lines are plotted using $E_k = -\hbar^2/2m_0\{Ak^2 \pm [B^2k^4 + C^2(k_1^2k_2^2 + k_2^2k_3^2 + k_3^2k_1^2)]^{1/2}\}$. The $-$ sign is used for heavy holes with $A = 4.60$, $B = 0.265$, and $C = 3.85$, and the $+$ sign is for the light holes with $A = 4.59$, $B = 0.256$, and $C = 3.81$.

## 3. Results and discussion

For both cases of $\Delta E_{s-o}(C) = 0$ and 6 meV, the light hole band results agree to within less than 1%. The light hole effective mass of GeC alloys increases monotonically from 0.078 $m_0$ for pure Ge to 0.19 $m_0$ for pure C (Fig. 2). The light hole value of C is similar to the previously reported value of 0.21 $m_0$ [17]. Although the light hole value of Ge is higher than the tabulated value of 0.044 $m_0$ [18], the qualitative behavior of GeC effective mass on alloy composition can be predicted. The quantitative values should be accurate only for the carbon rich side of the GeC alloys. The increase of light hole mass with carbon content ($x$) is linear initially and starts to saturate for $x > 0.3$. In the case of $\Delta E_{s-o}(C) = 0$ meV, the heavy hole effective mass shows a striking feature as the carbon concentration increases (Fig. 2). The calculated heavy hole mass of 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 [17]. The calculated heavy hole effective mass of Ge is 0.37 $m_0$, similar to previously calculated values of 0.36 $m_0$ [19] and 0.346 $m_0$ [20]. Although Ge has a lower heavy hole effective mass ($m_{hh}$) than C, $m_{hh}$ of $Ge_{1-x}C_x$ alloys decreases slightly (less than 5%) with the carbon concentration from 0 to $\sim 0.5$ and then increases slowly up to $x = 0.97$. Finally, an increase by a factor of 2 of heavy hole masses is found from $x = 0.97$ to pure C. In other words, if it starts from the carbon rich side, the effect of germanium is dramatic. A 0.5% of germanium incorporation into carbon causes a drop of about 60% of the difference between heavy hole mass values of the pure carbon and pure germanium. Similar results are also found in SiC alloys [21]. By using $\Delta E_{s-o}(C) = 6$ meV, the calculated $m_{hh}$ of pure carbon is 0.45 $m_0$ which is also within range of the

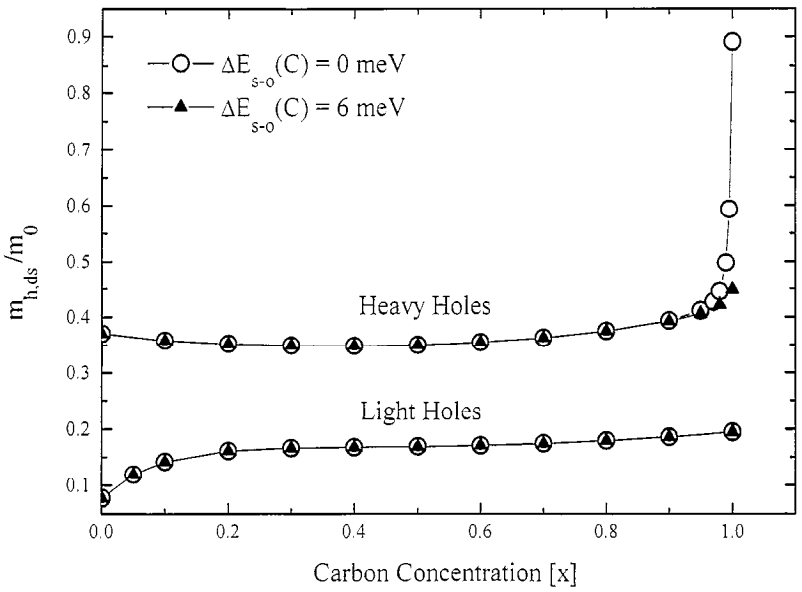


Fig. 2. Heavy hole and light hole effective masses of $Ge_{1-x}C_x$ alloys.

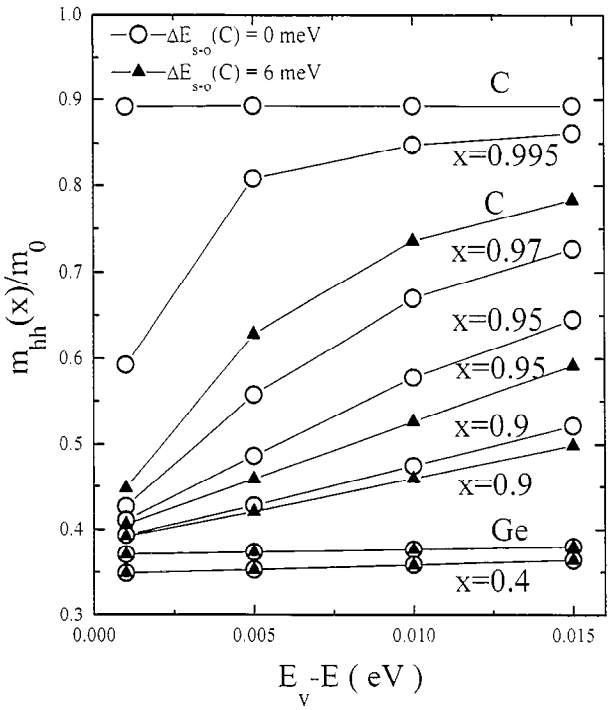


Fig. 3. Energy dependence of the heavy hole effective masses of $Ge_{1-x}C_x$ alloys.

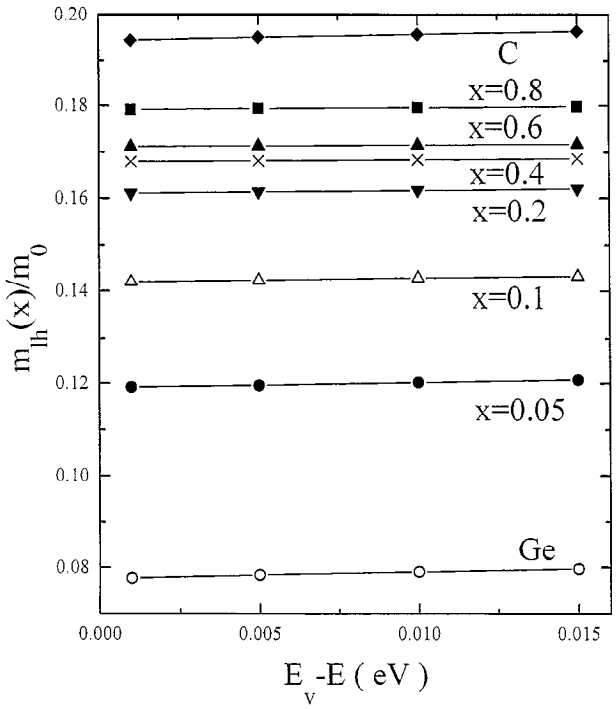


Fig. 4. Energy dependence of the light hole effective masses of $Ge_{1-x}C_x$ alloys for both $\Delta E_{s-o}(C) = 0$ and 6 meV.

previously reported values [17]. The heavy hole effective mass for the alloys are indistinguishable with those calculated using $\Delta E_{s-o}(C) = 0$ meV from $x = 0$ up to about $x = 0.9$ (Fig. 2). The increase of $m_{hh}$ from $x > 0.9$ to $x = 1.0$ is not as sharp as that found in the case of zero diamond split-off energy but shows a similar trend (Fig. 2). To study the non-parabolicity of the valence band structure, the heavy hole and the light hole effective masses are plotted as functions of hole energy in Figs. 3 and 4, respectively. The light hole masses of GeC alloys are relatively independent of hole energy. With $\Delta E_{s-o}(C) = 0$ meV, the heavy hole mass increases with hole energy in a complicated manner, depending on the C content. For $0 \leq x \leq 0.90$ and the extreme case of $x = 1.0$ (pure diamond), the dependence between heavy hole mass and hole energy is linear, but a highly non-linear behavior is observed for $0.95 \leq x \leq 0.995$. For the case with non-zero diamond split-off energy the energy dependence of heavy hole masses are less complicated, the non-linear behavior appears in the region of about $0.98 \leq x \leq 1.0$. The energy dependence of the effective masses of both heavy hole and light hole is analyzed by the equation $m(E) = m(0)(1 + \alpha E)$, where $\alpha$ is the non-parabolicity parameter. The $\alpha$ value of the light hole band is

1.9/eV for pure Ge, and decreases rather monotonically to 0.75/eV for pure C. In the case of $\Delta E_{s-o}(C)=0$ meV, the $\alpha$ values for the heavy hole bands vary over a wide range (Fig. 5). The $\alpha$ value is 1.8/eV for pure Ge and increases monotonically to 120/eV as the carbon concentration reaches 99%, and soon drops to 0.098/eV as the alloy becomes diamond. Note that the $\alpha$ values for $0.95 \le x \le 0.995$ are calculated using $m_{hh}$ values at 1 and 5 meV due to the fact that the energy dependence becomes nonlinear over this range. While taking $\Delta E_{s-o}(C)$ as 6 meV, the $\alpha$ values increase monotonically from 1.8/eV for pure Ge to 101/eV for pure C (Fig. 5). The energy band structure in Eq. (3) can be written in terms of an expansion over the anisotropic part [16]:

$$E_k \approx \frac{-\hbar^2}{2m_0}\left\{(A \pm B')k^2\left[1-\Gamma_{\pm} \times\left(\frac{1}{3}-\frac{\sin^4\theta(\cos^4\phi+\sin^4\phi)+\cos^4\theta}{2}\right)\right]\right\} \quad (5)$$

where $B'=\sqrt{B^2+C^2/6}$ and

$$\Gamma_{\pm}=\mp\frac{C^2}{2B'(A\pm B')}, \quad (6)$$

which indicates the anisotropy of the energy band (where the + sign is valid for the heavy hole band and the − sign for the light hole band). The anisotropy parameter $\Gamma$ is the measure of the deviation of energy contour from spherical band. The anisotropy $\Gamma$ as a function of the carbon concentration for 1 meV energy contour shows the effect of carbon incorporation on the shape of the constant energy surface (Fig. 6). The constant energy surface of light hole band changes moderately as the content of carbon increases and the anisotropy is relatively weak, compared to heavy hole bands. For the heavy hole band, in the case of zero diamond split-off energy, the $\Gamma$ value increases by a factor of about 3 from $x=0.97$ to pure carbon, indicating the large change of the constant energy contour when the $Ge_{0.03}C_{0.97}$ alloy turns into diamond. With $\Delta E_{s-o}(C)=6$ meV, the $\Gamma$ values coincide with those obtained from zero $\Delta E_{s-o}(C)$ from $x=0$ to about $x=0.9$ but the rise from $x>0.9$ to $x=1.0$ is less steep.

The origin of the anomalous effects in the heavy hole band properties near the carbon rich side of the alloys can be understood by the interaction between the heavy hole band and the split-off hole band [21]. In our calculation, the spin-orbital coupling strength $\xi$ was obtained to have the split-off energies of 0.0 and 6 meV for C and 290 meV for Ge, respectively. As a result, the $\Delta E_{s-o}$ of GeC alloys is a linear function of C content. In the case of $\Delta E_{s-o}(C)=0$ the incorporation of germanium into carbon, on top of changes of other parameters such as lattice constant, overlap integrations 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 bands. At small Ge concentration in the C, the split-off band is very close to the heavy hole band and the interactions between the two band edges are relatively stronger compared to the Ge rich case, where two band edges are rather far apart. For example, split-off energy of the $Ge_{0.005}C_{0.995}$ is about 1.45 meV, very close to the hole energy 1 meV where the nominal effective mass is evaluated. This causes a strong deformation of the heavy hole band near the band edge of $Ge_{0.005}C_{0.995}$ and thus the nominal effective mass deviates from the linear behavior dramatically. This accounts for the result of nonlinear energy dependence of $m_{hh}$ for $Ge_{1-x}C_x$ in the range of $0.95 \le x < 1.0$, where split-off energy is within 14.5 meV, comparable with the range of calculated hole effective mass (1–15 meV). In the case of $\Delta E_{s-o}(C)=6$ meV, $m_{hh}$ for pure C is lower than that found using $\Delta E_{s-o}(C)=0$ meV. It is, however, about the same as $m_{hh}$ for $Ge_{0.02}C_{0.98}$ which, given $\Delta E_{s-o}(C)=0$, has a split-off energy of about 6 meV. The non-linear energy depend-

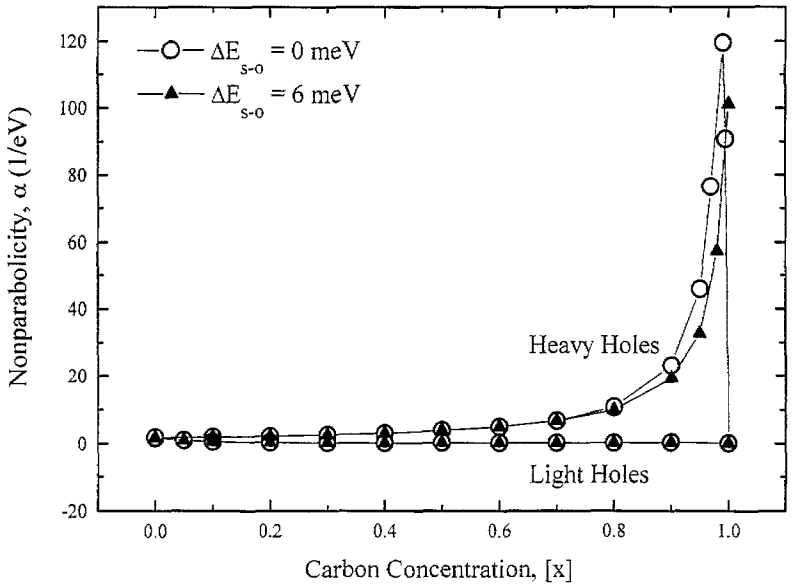


Fig. 5. Non-parabolicity parameter $\alpha$ of the heavy hole effective mass in $Ge_{1-x}C_x$ alloys.

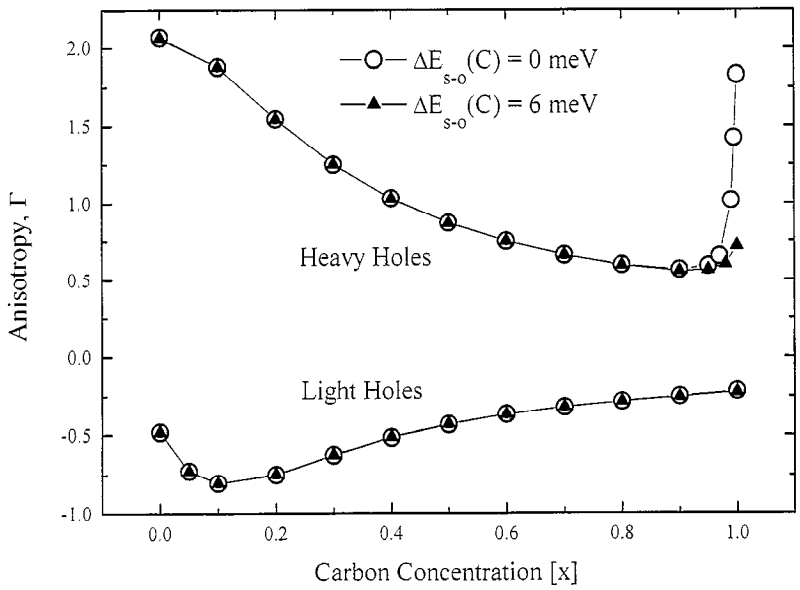


Fig. 6. Anisotropy parameter Γ of the heavy and light hole bands in $Ge_{1-x}C_x$. The hole energy is kept at 1 meV.

ence of $m_{hh}$ in the case of non-zero diamond split-off energy occurs in the range of $0.965 \leq x \leq 1.0$, where split-off energies are within 16 meV, comparable with the range of calculated hole effective mass (1–15 meV).

## 4. Summary

By observing the behaviors of heavy hole of GeC alloys and SiGe [21] alloys, 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. Moreover, this anomalous effect of hole effective masses has to be taken into account for the future device applications of GeC alloys.

## Acknowledgements

This work is supported by National Science Council of ROC under contract No. NSC85-2112-M-005-007 and No. NSC86-2112-M-005-013 (CYL), and No. NSC86-2215-E-002-0041 (CWL).

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