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δ doping in strained (Si)/(Ge) superlattices

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We present a comparative study of the pseudomorphic $(Si)_6/(Ge)_6$ and δ-doped $(Si)_3(Sb)(Si)_2/(Ge)_6$ superlattices using the self-consistent pseudopotential method. The strained $(Si)_6/(Ge)_6$ superlattice has the lowest conduction-band states of extended character, and the difference of energy between the direct and indirect band gap is 70 meV. Upon δ doping by Sb in the Si sublattice, a quasi-two-dimensional band confined to the Sb layer dips into the band gap. Furthermore, the average potential in the Ge sublattice rises relative to that of the Si side, which increases the band offset, and enhances the localization of the quantum well states. These results indicate that δ doping provides new means for controlling the electronic properties of strained superlattices.

Pseudomorphic $(Si)_n/(Ge)_n$ $(n \leq 6)$ superlattices laterally restricted to the Si(001) surface have been grown[1] in spite of the large lattice mismatch (4%) of constituent crystals. Recent studies[1-6] on these semiconductor heterostructures have revealed novel electronic properties. It was shown that the band lineup is strongly dependent on the lattice strain.[2,6] In $(Si)_n/(Ge)_n$ $(3 < n \leq 6)$ the valence band of the Ge sublattice rises relative to that of the Si sublattice leading to a band offset[2] $\Delta E_V = E_{V,\mathrm{Ge}} - E_{V,\mathrm{Si}}$, of 0.84 eV. As a result carriers (electrons and holes) are separated in real space. While electrons are confined in the Si sublattice, holes are localized in Ge displaying a staggered type-II alignment. Most importantly, direct optical transitions have been observed,[1] which are found neither in constituent crystals, nor in $Si_{1-x}Ge_x$ alloys. Currently, modifying the electronic structure of Si by varying the structural parameters of a strained superlattice $[(Si)_{1-x}(Ge)_x]_n/[(Si)_{1-y}(Ge)_y]_m$, and thus improving its electronic properties, has been extensively studied.[6] In an effort to incorporate optoelectronics into the Si-based microelectronics, the possibility of obtaining a direct-band semiconductor using a (Si)/(Ge) heterostructure has become a topic of major interest. A small oscillator strength of the lowest direct transition and the stability of the heterostructure seem to present significant difficulties, however.

An alternative way to control the band alignment and, thus, to modify the confined states in the (Si)/(Ge) quantum-well structure may be to incorporate an extremely sharp and high-density doping profile. This type of doping is called δ doping.[7] An early suggestion that the band offset of a semiconductor heterostructure can be modified was demonstrated for the first time by Capasso, Cho, Mohammed, and Foy[8] for $Al_xGa_{1-x}As/GaAs$ heterojunction. A new type of nonalloyed Ohmic contact with GaAs is achieved by placing a high-density donor sheet a few layers away from the metal-semiconductor interface.[9] Zeindel *et al.*[10] have incorporated a sheet of Sb into Si(001) with an aerial density of $\sim 1.6\times 10^{13}$ Sb cm^{-2}. They showed that this δ layer gives rise to a quantum well with the confined states of electrons.

The δ doping is rather different from the modulation doping or bulk doping of Si. Upon the growth of a high-density impurity sheet the excess carriers due to the impurity atom are confined in the quantum well of the "finite" δ layer, and give rise to the two-dimensional (2D) subband structure. If the thickness of the δ layer is reduced to a single layer, the impurity states may be delocalized and form a two-dimensional (2D) band restricted to this layer. The delocalization of impurity states and dispersion of the bands produced therefrom have to be dependent on the concentration of the dopant, and, thus, on the overlap of nearest-neighbor impurity orbitals $\langle \phi_i(\mathbf{r}) | \phi_i(\mathbf{r}+\mathbf{D}) \rangle$. While the impurity band modifies the band gap, the charge distribution and the potential at the δ layer may affect the band diagram of the heterostructure. The form of the band diagram and the stability of the δ layer against the exchange-place reaction have to vary according to its position. Therefore, significant variances are anticipated depending upon whether the δ layer is located at the interface or in one of the sublattices. The thickness and the impurity concentration of the δ layer are also crucial parameters which influence the electronic structure.

We have investigated the effect of the δ layer on the pseudomorphic $(Si)_n/(Ge)_n$ superlattices. In this paper, we present a comparative study of strained $(Si)_6/(Ge)_6$ and δ-doped $(Si)_3(Sb)(Si)_2/(Ge)_6$ both restricted to the Si(001) surface. The δ layer here is idealized with one Sb atomic plane replacing the fourth Si plane in the unit cell

of $(Si)_6/(Ge)_6$, and is used only to explore its effect on the electronic structure of the (Si)/(Ge) superlattices. The important findings of our study are (i) the average potential of the Ge sublattice rises relative to that of Si, which in turn increases the depth of the quantum well structure, and thus enhances the localization of the confined states, and (ii) the lowest conduction-band state of $(Si)_6/(Ge)_6$, which have almost equivalent weights in both sublattices (Si and Ge), are replaced by a quasi-2D band confined to the Sb layer. It is shown that the inclusion of an ultrathin dopant layer can modify the band lineup of the strained (Si)/(Ge) superlattice.

We have performed total-energy and charge-density calculations for $(Si)_6/(Ge)_6$ and $(Si)_3(Sb)(Si)_2/(Ge)_6$ by using the standard self-consistent field (SCF) pseudopotential method with nonlocal, norm-conserving pseudopotentials[11] and Ceperley-Alder exchange correlation approximation.[12] Other details about the method can be found elsewhere.[13] Bloch states are expanded in terms of $\sim$1500 plane waves corresponding to a kinetic energy cutoff of $|\mathbf{k}+\mathbf{G}|^2 \leq 13.5$ Ry. To ensure the epitaxy, the lateral lattice constants are set equal to those of the ideal Si(001) surface [$|\mathbf{R}_1| = |\mathbf{R}_2| = a_0(\mathrm{Si})/\sqrt{2}$, $a_0(\mathrm{Si})$ being the equilibrium lattice constant of bulk Si]. The equilibrium lattice constant of bulk Si is calculated to be 10.24 a.u. The perpendicular lattice constants of $(Si)_6/(Ge)_6$ are determined by minimizing the total energy with respect to the structural degrees of freedom. These are the Si-Ge and strained Ge-Ge interlayer spacings. The superlattice formation energy of $(Si)_6/(Ge)_6$, ΔE^f, is calculated from the total energies, E_T and E_T^0, of the superlattice and constituent crystals, respectively,

$$\Delta E^f((\mathrm{Si})_6/(\mathrm{Ge})_6) = E_T((\mathrm{Si})_6/(\mathrm{Ge})_6) - [E_T^0((\mathrm{Si})_{12}) + E_T^0((\mathrm{Ge})_{12})]/2 ,$$

and is found to be 9.29 mRy/cell favoring the separation into constituent crystals. This structure is metastable because the activation energy either for segregation or for the generation of the misfit dislocation is larger than ΔE^f $(n=6)$. The interfacial energy of the Si-Ge interface is calculated to be $\sim$0.5 mRy. The strain energy stored in the Ge sublattice, which dominates ΔE^f, is found to be proportional to n, and is 1.46 mRy per Ge atom. Therefore, $\Delta E^f(n)$ increases with increasing n. In $(Si)_3(Sb)(Si)_2/(Ge)_6$, the interlayer spacing between the adjacent Si and Sb atomic planes is fixed to the sum of the covalent radii of Si and Sb. Other structural parameters [the lateral lattice constants of the (001) cell, $|\mathbf{R}| = |\mathbf{R}| = 7.24$ a.u.; the interlayer spacing in the Si sublattice, d(Si-Si)=2.56 a.u.; the interlayer spacing at the interface, d(Si-Ge)=2.60 a.u.; and the interlayer spacing in the Ge sublattice, d(Ge-Ge)=2.70 a.u.] are taken to be the same as in $(Si)_6/(Ge)_6$.

Having determined the structural parameters we discuss the electronic structure of $(Si)_6/(Ge)_6$. The SCF pseudopotential method within the local-density approach underestimates the conduction-band energies. However, the average error in bulk Si and Ge is $\sim$0.5 eV for the kinetic energy cutoff, $|\mathbf{k}+\mathbf{G}|^2 \leq 13.5$ Ry. Therefore, the present study is extended to explore the electronic structure of the superlattices by applying a constant upward shift of 0.5 eV to the conduction-band energies. Using the same approach[3] we calculated that the indirect band gap of the strained $(Si)_4/(Ge)_4$ is 0.8 eV. The value for the same energy gap obtained from the local-density-functional and quasiparticle self-energy calculations by Hybertsen and Schlüter[5] is 0.85 eV. An important character of the electronic structure, that is, the difference in the indirect and direct energy gap δE_g, is affected by the zone folding[14] and the lattice[2-4] strain. Bands along the δ direction of the cubic Brillouin zone (CBZ) are folded for $\mathbf{k}\parallel[001]$ (or $k_\perp$) resulting in a decrease of δE_g. In contrast, the bands at the top of the valence band are split and the lowest conduction band at $\mathbf{k}=\mathbf{0}$ rises under the tetragonal strain of Ge, the net effect being an increase of δE_g in the strained Ge. Finally, upon formation of $(Si)_6/(Ge)_6$ the bands of the sublattices shift leading to the quantum wells with the flat conduction bands along the superlattice direction. While the states of these conduction bands are confined in the Si sublattice, first and second highest valence-band states are weakly localized in Ge. In Fig. 1, we present the contour plots of the total- and state-charge density for $(Si)_6/(Ge)_6$. The quantum-well structure deduced from the localization of the states suggests that electron and hole quantum wells are located in Si and Ge, respectively. Because of the small electron mass and the small size of the quantum well, the states of the lowest conduction band for $\mathbf{k}$ [$k_\perp=0, \mathbf{k}\parallel\Delta$, or ΓM direction of the superlattice Brillouin zone (SBZ)] have an extended character, however. While the lowest direct

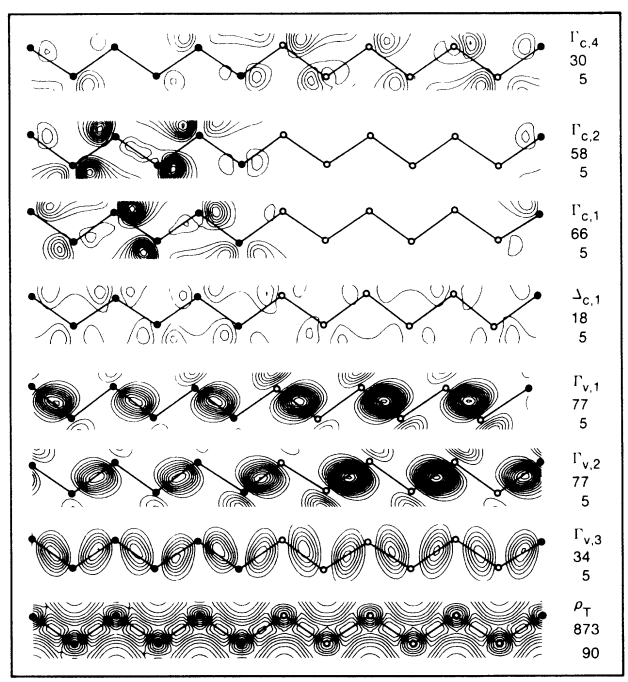

FIG. 1. Contour plots of the total- and state-charge density of $(Si)_6/(Ge)_6$. ρ_T is the total-charge density. $\Gamma_{v,1}$ and $\Gamma_{c,1}$ denote the topmost valence and the lowest conduction-band states at the Γ point, respectively. Upper and lower numerals indicate the value of the maximum charge density (in 10^{-4} $\times$electrons$\times$bohr^{-3}) and contour spacings, respectively.

transition $\Gamma_{v,1} \rightarrow \Gamma_{c,1}$ occurs at 0.84 eV with a small oscillator strength, the lowest value of the band gap is 0.77 eV between Γ_v and $\Delta_{c,\min}$. Accordingly, the energy gap of the $(Si)_6/(Ge)_6$ superlattice is found to be indirect ($\delta E_g > 0$). A more significant finding, however, is that the energy separation between the direct and indirect band gap of Si decreases from ~ 2 to 0.07 eV.

The integration of the planarly averaged charge density

$$\bar{\rho}(z) = \frac{2}{a_0^2} \int_0^{a_0\sqrt{2}} \int_0^{a_0\sqrt{2}} \sum_{n,k}^{E \le E_F} |\psi_n(\mathbf{k},\mathbf{r})|^2 dx\, dy$$

between two consecutive atomic (001) planes, l and $l+1$,

$$q(l+1,l) = \frac{a_0^2}{2} \int_l^{l+1} \bar{\rho}(z) dz$$

shows small deviations from the ideal bulk value (4 ± 0.02 electrons). This implies that the transfer of charge upon superlattice formation is rather small.

The question we shall address next is how the electronic structure of the $(Si)_6/(Ge)_6$ superlattice is modified when one Si atomic layer (i.e., fourth layer in the unit cell) is replaced by Sb. The amount of electronic charge between the adjacent $(Si)_3$-(Sb) and (Sb)-$(Si)_5$ (001) atomic planes is found to be 4.51 and 4.56 electrons per atom. These self-consistent values of $q((Si)_3,(Sb))$ and $q((Sb),(Si)_5)$ indicate that the simple bond picture predicting the excess charge of $Q = -e(Z-4)/2$ (Z being the valency of the dopant atom) is approximately valid, except for a small deviation of 0.07 electrons. On the other hand, we calculated that a small amount of charge is transferred from one side $[(Si)_3(Sb)(Si)_2]$ to the adjacent Ge side of the superstructure, which leads to a relative shift in the average potential energies $\bar{V}$ of two sublattices.

The potential, consisting of the local part of the ionic pseudopotential, Hartree, and exchange potentials, are planarly averaged and, thus, the 1D potential $\bar{V}(z)$ is generated. The average of $\bar{V}(z)$ is calculated in the adjacent sublattices $\bar{V}_{Si}$ and $\bar{V}_{Ge}$. The difference of the average potentials $\bar{V}_{Si}$-$\bar{V}_{Ge} = \Delta V$ is found to decrease by 90 meV upon δ doping, implying that the electronic states of the Ge sublattice rise (or those of the Si sublattice are lowered). This causes the band offset, ΔE_V, of $(Si)_6/(Ge)_6$ to increase from 0.84 to 0.93 eV upon the δ doping. As a result, the depth of the quantum well (for both electron and hole) increases, but the band gap of the superlattice decreases. The effect of the relative shift in the average potential energies of the sublattices, ΔV, is seen in the charge density and electronic band structure of $(Si)_3(Sb)(Si)_2/(Ge)_6$.

The contour plots of the total- and state-charge density for $(Si)_3(Sb)(Si)_2/(Ge)_6$ are shown in Fig. 2. The localization of the states at the top of the valence band are significantly increased as compared to those of $(Si)_6/(Ge)_6$ illustrated in Fig. 1. The extended states of $(Si)_6/(Ge)_6$ along the Δ direction and near the X point of the CBZ with $\mathbf{k} \parallel (001)$ are replaced by a quasi 2D band of the δ layer, and become localized on the $(Si)_3(Sb)(Si)_2$ side. Along the ΓZ direction of SBZ the first and second conduction-band states are also confined to the Si side, and their charge distributions do not differ significantly

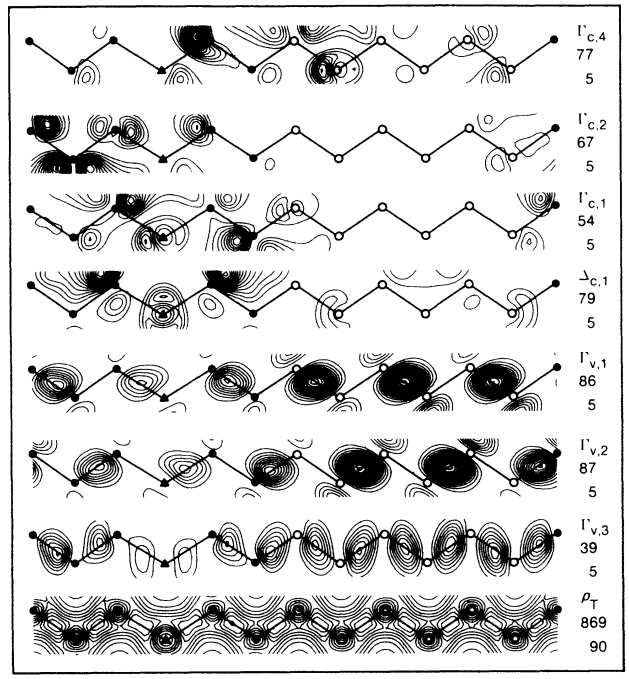

FIG. 2. Contour plots of the total- and state-charge density of $(Si)_3(Sb)(Si)_2/(Ge)_6$.

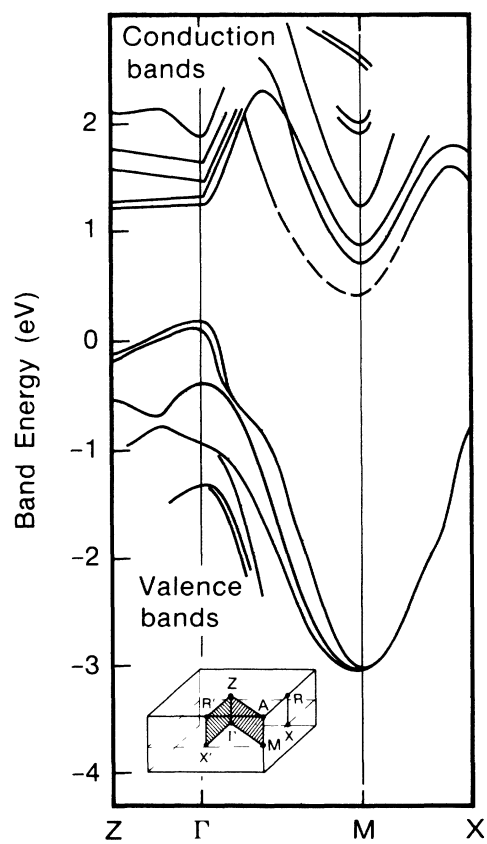

FIG. 3. Energy band structure of $(Si)_3(Sb)(Si)_2/(Ge)_6$. The zero of energy is set to the average energy of the topmost three valence-band states. The inset shows the superlattice Brillouin zone, where the ΓM direction corresponds to the Δ direction of CBZ. The 2D band originating from the δ layer is shown by dashed lines.

from those of $(Si)_6/(Ge)_6$. These states are derived from the Si sublattice. Similarly, the third conduction-band state is localized at the interface and in the Ge sublattice. However, the fourth conduction-band state has a strong weight near the Si−Sb−Si bonds, and is associated with the δ layer.

The band structure of $(Si)_3(Sb)(Si)_2/(Ge)_6$ in Fig. 3 displays the minizone with flat bands for $\mathbf{k}_\perp$ (shown in the ΓZ direction). In contrast to $(Si)_6/(Ge)_6$ the lowest conduction band along the ΓM direction is lowered and has a minimum at the M point of SBZ. Owing to factors such as the lowering of the lowest conduction band and the band energies of the Ge sublattice, the indirect band gap is decreased. Certainly, the effects of those factors on the band gap is proportional to the concentration of the dopant. In the present study the Sb monolayer has maximum concentration (or minimum Sb-Sb distance), and thus the largest effect in reducing the band gap. Since the excess charge $(Z-4)$ is one electron per cell, the Fermi level crosses the conduction band rendering the metallization of the superlattice. However, at comparatively lower dopant concentration, the occupancy of the lowest conduction band is significantly reduced. Recently, Zeindl *et al.*[10] simulated the Sb sheet, which they incorporated in the Si(001) sample, by Sb^+ ions uniformly distributed in a ~20-a.u.-thick slab leading to a quantum well. They carried out self-consistent calculations within the effective mass approximation, and obtained four subbands. Since the plane of Sb atoms in the present model cannot be treated as a quantum well, our states associated with the δ layer are not comparable with these subbands. However, our results show similar trends, such as the lowering of the band gap and localization of the lowest conduction-band states at the Sb layer.

In conclusion, we have shown that a monolayer of Sb lattice matched to the Si sublattice in a pseudomorphic $(Si)_6/(Ge)_6$ superlattice leads to important changes in the electronic structure. The monolayer doping is only an idealized model, and is unstable as far as the energy of formation is concerned. It gives rise to a quasi 2D metallic band, and increases the band offset. While the δ doping with high dopant concentration and finite thickness provides Ohmic contacts, it can also be used to alter the electronic properties of heterostructures, and to obtain new device characteristics at comparatively lower dopant concentrations.

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[1]T. P. Pearsall, J. Bevk, L. C. Feldman, J. M. Bonar, J. P. Mannaerts, and A. Ourmazd, Phys. Rev. Lett. **58**, 729 (1987).

[2]C. G. Van de Walle and R. M. Martin, J. Vac. Sci. Technol. B **3**, 1256 (1985).

[3]S. Ciraci and I. P. Batra, Phys. Rev. Lett. **58**, 2114 (1987); S. Ciraci and I. P. Batra, Phys. Rev. B **38**, 1835 (1988); S. Ciraci, O. Gülseren, and Ş. Ellialtioglu, Solid State Commun. **65**, 1285 (1988).

[4]S. Froyen, D. M. Wood, and A. Zunger, Phys. Rev. B **36**, 4574 (1987); R. People and S. A. Jackson, *ibid.* **36**, 1310 (1987); I. Morrison and M. Jaros, *ibid.* **37**, 916 (1988).

[5]M. S. Hybertsen and M. Schlüter, Phys. Rev. B **36**, 9683 (1987); L. Brey and C. Tejedor, Phys. Rev. Lett. **59**, 1022 (1987).

[6]G. Abstreiter, H. Burgger, T. Wolf, H. Jorke, and H. Herzog, Phys. Rev. Lett. **54**, 2441 (1985).

[7]D. Streit, R. A. Metzger, and F. G. Allen, Appl. Phys. Lett. **44**, 234 (1984).

[8]F. Capasso, A. Y. Cho, K. Mohammed, and P. W. Foy, Appl. Phys. Lett. **46**, 664 (1985).

[9]E. F. Schubert, J. E. Cunningham, W. S. Tsang, and T. H. Chiu, Appl. Phys. Lett. **49**, 272 (1986).

[10]H. P. Zeindl, T. Wegehaupt, I. Eisele, H. Oppolzer, H. Resinger, G. Tempel, and F. Koch, Appl. Phys. Lett. **50**, 1164 (1987).

[11]C. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 419 (1982).

[12]D. M. Ceperley and B. J. Adler, Phys. Rev. Lett. **45**, 566 (1980).

[13]The details of the calculations and references related to the method can be found in I. P. Batra, S. Ciraci, G. P. Sirivastava, J. S. Nelson, and C. Y. Fong, Phys. Rev. B **34**, 8246 (1986).

[14]L. Esaki and R. Tsu, IBM J. Res. Dev. **14**, 61 (1970).