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PREDICTED MODIFICATIONS IN THE DIRECT AND INDIRECT GAPS OF Si

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We have studied the effects of expansion of the lattice on fundamental band gaps in Si, with the use of an adjusted pseudopotential method. The results show that Si structure becomes a direct band gap. A correlation is given with the properties of tetrahedrally filled semiconductors and those of porous silicon.

Keywords: A. semiconductors, D. electronic band structure, D. electronic stakes (localized).

1. INTRODUCTION

RECENT observation of photoluminescence in porous silicon at room temperature [1] has stimulated a great deal of interest in studying the origin of visible luminescence in porous silicon. Therefore, there has been a revival of interest in ways to create a silicon structure with a direct band gap. Bulk silicon has indirect band gap, which under normal circumstances prevents efficient interband radiative recombination. If the optical properties of silicon become as useful as the electronic properties, the popular semiconductor would play as large a role in the emerging technology of optoelectronics as it has in the microelectronics revolution. Thus the understanding of the optical properties of direct band gap silicon is important and the results may be a powerful prediction of the properties of porous silicon. Many experimental and theoretical investigations have been devoted to this goal, and several conjectures of the origin of this visible light emission have been proposed.

The first is the investigation of silicon where the cubic symmetry is broken and the zone-edge states are folded back to the center of the zone [2-4]. The second area focuses on predicting the properties of silicon with the diamond structure [5, 6]. This in effect alters the chemical and structural environment of the bulk material in a uniform way. Here we consider the latter approach and attempt to provide a theoretical base for further studies of this material.

At each stage the introduction of new materials and

growth techniques has allowed new physical effects and led to significant advances in semiconductor applications. The growth of strained-layer structures should have several advantages. Strained layers allow for new materials combinations on established substrates. With the independent variation of band gap and lattice constant, it is possible to access new band regimes not otherwise achievable with III-V semiconductors.

Thin strained layer superlattices have recently emerged as a possible candidate for the creation of direct gap materials from constituents that have indirect gaps. This is of great importance because it could lead to new optoelectronic devices based on Si, Ge, GaP, AlAs, AlSb,... which are indirect gap semiconductors, and are also the most technologically developed electronic materials.

In this work we will examine the way to alter the direct vs indirect nature of the lowest optical gaps. Defining the "degree of indirectness" $\delta = 2(E_D - E_i)/(E_D + E_i)$ in terms of the direct (E_D) and indirect (E_i) , evaluated at the X point in the Brillouin zone) band gaps, we will determine whether indirect gap Si, can be made direct $(\delta < 0)$ by lattice expansion effects, rather by conventional substitutional insertion (e.g., alloying indirect gap Si with direct gap Sn).

We will then demonstrate how insights deduced from simple and (so far) hypothetical applied negative pressure can predict a new class of direct-gap semiconductors. In this study the charge densities and eigenvalues are obtained by solving the one-particle Schrödinger equation. The empirical pseudopotential method [7] is used in order to investigate the effects of cell volume on the size of the energy gap.

2. CALCULATIONS

Let us define our empirical pseudopotential parameters (EPP) of a semiconductor as a superposition of the pseudo-atomic potential of the form $V(\mathbf{r}) = V_L(\mathbf{r}) + V_{NL}(\mathbf{r})$, where V_L and V_{NL} are local and nonlocal parts, respectively. In this calculation we have omitted the nonlocal part.

We regard the Fourier components of $V_L(\mathbf{r})$ as the EPP local parameters.

We determine the EPP parameters by the nonlinear least squares method, in which all the parameters are simultaneously optimized under a defined criterion of minimizing the root-mean square (rms) deviation. The experimental electronic band structure at normal and under pressure data are used.

Our nonlinear least squares method requires that the r.m.s.-deviation of the calculated level spacings (LS) from the experimental ones defined by

$$\delta = \left[\sum_{(i,j)}^{m} [\Delta E^{(i,j)}]^2 / (m-N) \right]^{1/2}$$
(1)

should be minimum

$$\Delta E^{(ij)} = E \exp^{(i,j)} - E_{\text{calc}}^{(i,j)}$$

where $E \exp^{(i,j)}$ and $E_{calc}^{(i,j)}$ are the observed and calculated LSs between the *i*th state at the wave vector $\mathbf{k} = \mathbf{k}_i$ and the *j*th at $\mathbf{k} = \mathbf{k}_j$, respectively, in the *m* chosen pairs (i,j). *N* is the number of the EPP parameters. The calculated energies given by solving the EPP secular equation depend nonlinearly on the EPP parameters. The starting values of the parameters are improved step by step by iterations until δ is minimized. Let us denote the parameters by P_u (u = 1, 2, ..., N) and write as $P_u(n+1)P_u(n) + \Delta P_u$, where $P_u(n)$ is the value at the n^{th} iteration. These corrections ΔP_u are determined simultaneously by solving a system of linear equations

$$\Sigma_{u=1}^{N} [\Sigma_{(i,j)}^{m} (Q_{u}^{i} - Q_{u}^{j}) (Q_{u'}^{i} - Q_{u'}^{j})] = \Sigma_{(i,j)}^{m} [E_{exp}^{(i,j)} - E_{calc}^{(i,j)}(n)] (Q_{u'}^{i} - Q_{u'}^{j}), \qquad (2)$$
$$u' = (1, ..., N)$$

where $E_{calc}^{(i,j)}(n)$ is the value at the *n*th iteration, Q_u is given by

$$Q_{\mathbf{u}}^{j} = \Sigma_{q,q'} [C_{q}^{i}(\mathbf{k}_{i})]^{*} [\partial H(\mathbf{k}_{i})/\partial P_{\mathbf{u}}]_{qq'} C_{q'}^{i}(\mathbf{k}_{i}).$$
(3)

 $H(\mathbf{k}_i)$ is the pseudo-Hamiltonian matrix $\mathbf{k} = \mathbf{k}_i$ in the plane wave representation, and the *i*th pseudo-wave function $\mathbf{k} = \mathbf{k}_i$ is expanded as

$$\psi_{\mathbf{k}i}^{i}(\mathbf{r}) = \Sigma_{q} C_{q}^{i}(\mathbf{k}_{i}) \exp[i(\mathbf{k}_{i} + \mathbf{k}_{q})\mathbf{r}], \qquad (4)$$

 \mathbf{k}_q being the reciprocal lattice vector. Equation (2) shows that all of the parameters are determined automatically in an interdependent way.

In our calculation we have used five pairs of states \mathbf{k}_i and \mathbf{k}_j : $(\Gamma - \Gamma)$, $(\Gamma - X)$, $(\Gamma - L)$, (X - X), (L - L), which corresponds to five LSs. The dimension of our eigenvalue problem is a (136, 136) matrix. However, 59 plane waves give a good convergence.

The resulting pseudo-wave-functions $\Psi_{n\mathbf{k}}(\mathbf{r})$, which are obtained once the pseudopotential form factors are adjusted, are used to compute the total valence charge density according to the following expression (*n* is the band index and **k** stands for wave vectors):

$$\rho_n(\mathbf{r}) = e \Sigma_n \Sigma_{\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 \tag{5}$$

Since we are not interested in the total valence charge density in the whole Brillouin zone, but at the high symmetry points in this zone for specific band. Thus

$$\rho_n(\mathbf{r}) = e |\psi_{n\mathbf{k}}(\mathbf{r})|^2 \tag{6}$$

with $\mathbf{k} = 2\pi/a(0,0,0)$ stands for the Γ point and $\mathbf{k} = 2\pi/a(1,0,0)$ for the X point (a is the lattice constant), and n is equal to 5 or 6 for the first conduction band or the second conduction band respectively.

3. RESULTS

Table 1 gives the adjusted pseudopotential form factors of Si which give a reasonable agreement with experiment for the principal energy gap (Table 2). Figures 1 and 2 display the band structure at different pressure and the variation of the different band gaps with lattice constant variations for Si respectively. At the equilibrium volume, the band gap is indirect from Γ to $X(\delta = 0.90)$.

The indirect gap first increases with volume until the Γ state crosses the X state. At around $V/V_0 = 1.17$ which corresponds to a lattice constant equal 5.728 Å the gap becomes direct at Γ . For Si, there exists a range of volumes where the gap is direct. The volume at which the gap becomes direct, however corresponds

Table 1. The adjusted local pseudopotential form factors $V_L(|\mathbf{G}|^2)$

	V(3) in Ryd	V (8) in Ryd	V (11) in Ryd
Si	-0.236348	0.05583	0.067471

Table 2. Comparison of the calculated energy levels spacing (in eV) of Si with experiment and other calculations

	Si				
	EPM (a)	CPA (b)	Cal	Exp	
$\Gamma_{15}^c - \Gamma_{25}^v$	3.40	3.43	3.39	3.4(c), 3.37(d)	
$X_{1}^{c} - \Gamma_{25}^{v}$	1.17	1.34	1.28	1.3 (d)	
$L_1^c - \Gamma_{25}^v$	2.23	2.24	2.01	2.01 (e),2.1 (f)	
$\Delta - \Gamma_{25}^v$		1.11	1.142	1.17 (c),1.15 (d)	

to a negative pressure of about -160 Kbar. One approach to achieving a larger volume is to grow several layers of Si on a substrate which forces the crystal to have a large lattice constant. A suitable substrate will be A1P (4.77 Å) which is large enough. However, it is also likely that on any substrate the highly strained lattice would relax via dislocations after several layers are grown [8–10]. This situation could be overcome as it has been shown recently, by a misorientation of the substrate [11].

Despite the fact that the large volume required to



Fig. 1. (a) The silicon band structure at normal (solid lines) and under positive pressure (dashed lines). (b) The silicon band structure at normal (solid lines) and under negative pressure (dashed lines).



Fig. 2. The calculated values of the $E_{\Gamma\Gamma}$, $E_{\Gamma\chi}$ and $E_{\Gamma L}$ gaps plotted as function of lattice expansion for Si (the dashed vertical line corresponds to the equilibrium lattice parameter).

create direct gap in Si is probably difficult, there is still interesting and potentially useful properties of Si from this study. For example, there is one noticeable feature in the variation of Si levels with pressure. First, at high enough volume the gap will close and the system will metallize. This corresponds to metallization at a large negative pressure, in contrast to the usual process of metallization which occurs at positive pressure due to the $\Gamma - X$ overlap [12–14].

Diamond Si is the most loosely packed structures consistent with the tetrahedral coordination for both types of atoms. Their openness is highlighted by the fact that the ratio of the volume of touching atomic spheres to that of the unit cell is 0.34, less than half of that for the close-packed element structures (0.74). These homeoctect structures may be characterized by the existence of four vacant (V) lattice sites (holes) at the tetrahedral interstitial sites nearest both Si atoms (sites V Si), both at the normal nearest-neighbour tetrahedral distance. Hence, as we traverse the < 111 > body diagonal in the Si, with the origin, say, at the atom site Si (0, 0, 0), we encounter the other Si at (1/4, 1/4, 1/4), the V sites at (1/2, 1/2, 1/2) and (3/4, 1/2)3/4, 3/4), both unoccupied in normal tetrahedral Si. We may structurally designate this arrangement as VSiSiV. Therefore, it can be affected by diffusion of interstitial impurities (e.g. H, He and Li), occupying the Vs sites. We refer to the structures with partially or completely occupied Vs sites as "filled tetrahedral compounds" [15-24].

Recent interest in the modifications of the elec-

tronic band structures of tetrahedral semiconductors by interstitial impurities has renewed effort to obtain detailed analyses of the topologies of electron charge densities at selected high symmetry **k** points along the conduction band edge of these materials [17-29]. Such charge distribution has been shown to depend strongly on the particular **k** point under consideration. For example, the charge densities at the X point of the conduction-band edges (X^c) of Si [30], Ge [15], GaAs [25, 26], ZnSe [27] differ considerably from those at L^c or Γ^c . These charge densities at selected **k** point can then be decomposed into *s*-, *p*-, and *d*-orbital contributions, and the information is used to analyze the observed differences along the charge-density topologies at the Γ and X **k** points.

Hence, in our calculations the presence of He atoms will be manifest not by where valence electrons are found, but rather by where they are not found. The problem of finding the changes induced in the electronic structure by insertion of He atoms in the empty interstitial sites is now mapped into a more transparent problem of calculating the response of the host electronic structure to electron-repelling potential wells at these sites.

With this formulation of the problem, it is straightforward to understand the potential susceptibility of diamond materials to band modification by insertion of closed-shell atoms at the interstitial sites. The high tetrahedral symmetry, but different content, of the occupied Si sites in the (highly directional- sp^3 -bonded diamond material implies very different, quite Vol. 96, No. 4

spatially inhomogeneous charge distributions for Bloch states $\psi_{n\mathbf{k}}(\mathbf{r})$ for different high symmetry points in the Brillouin zone, unlike the roughly uniform valence charge density for e.g., s electron in metals. Moreover, the vacant interstitial Vs sites possess the same high symmetry, and perturbing potentials centered on these sites will selectively affect band associated primarily with these sites. One expects the principal effect of insertion of a closedshell atom on a given state to be simply expulsion from the Pauli exclusion volume of its contribution to the valence charge density. These circumstances raise the possibility that filling the tetrahedral sites will have a chemically specific, selective effect on certain bands.

The emphasis above on sites and excluded volume makes it natural to seek an explanation in the charge densities for the relevant states. Whereas the charge densities of the occupied (bonding) bands at Vs are small, even a minor rearrangement can have a major effect on their antibonding (i.e. conduction band) counterparts. In Fig. 3 we display for Si the pseudocharge density in the (110) plane for the lowest conduction bands at Γ_c^{15} and $X(X_c^1)$. We see that at the conduction band Γ_c [Fig. 3(a)] the electron charge is anti-bonding-like with a nodal plane intersecting the internuclear axis connecting the Si atoms. This charge distribution is predominantly s-like, most of the charge is localized on the ion sites. The situation at X however, is dramatically different since it contains a significantly higher d contribution and thus the electronic charge density is more delocalized. Finally, there is a buildup of charge density in the interstitial region (Fig. 3).

Therefore, these figures suggest the lowest conduction band will show extreme selectivity with respect to insertion of closed-shell atoms: the X_c^1 band density has maxima at or near Vs sites, whereas the Γ_c^{15} band has a much smaller Vs charge-density disparity. Therefore, because of the extremely high pseudo charge density at the Vs for the X_c band, but not for the Γ_c states, if we insert He atom at Vs (yielding what we call HeSiSiHe) will selectively shift to higher energies the X_c , conduction band more than do the other bands, exposing the Γ_c^1 point as the conductionband minimum.

The system has become a direct-gap material thus insertion of He dramatically reduces the indirectness parameter δ by a comparable amount for Si (changes in δ of -0.98) [30], converting Si into a slightly direct-gap material (since its theoretical initial $\delta = 0.9$).

The foregoing analyses indicates that the directness of the band gaps can be enhanced by placing electron repelling objects in the tetrahedral interstitial sites where the lowest conduction band has a higher electron density than other bands and hence is selectively shifted upwards. Comparatively, the modelling of the lattice expansion effect on the band structure of Si (as seen in Fig. 2) shows the same effect as those produced by insertion of He. Since, as we observed in Fig. 1, the X_c state is raised, whereas the Γ_c state is lowered, thus transforming Si to a direct material. Therefore, we may then conclude that the effect of inserting He will produce a lattice expansion. This assumption is supported by the work of Wood et al. [30] who found that insertion of He into the two interstitial sites in Si dilates the lattice by 3.9%, which corresponds to a lattice constant of 5.61 Å.

A comparison of the effect of lattice expansion and those of He, shows that for a lattice parameter of Si equal 5.61 Å, which corresponds to a negative pressure of 110 Kbar, δ is equal to -0.23, whereas according to Wood *et al.* [30] the effect of inserting He produces a material with $\delta = 0.08$, this result has





Fig. 3. (a) The calculated pseudocharge densities for the first conduction band in Si at the Γ point in the (110) plane at normal pressure. (b) The calculated pseudocharge densities for the first conduction band in Si at the X point in the (110) plane at normal pressure.

been obtained by the LDA [31, 32]. We know that the LDA produce gaps which are not consistent with the experimental results. Therefore, we think that our results $\delta = 0.23$ is within the LDA uncertainty (0.15). Therefore a strong correlation is noticed between insertion of interstitial impurities at the tetrahedral vacant sites and the effect of negative pressure. We may then conclude, that in order to produce negative pressure, it is possible to insert He. The experimental preparation of this new class of semiconductors does not appear at the present easy. On the above assumptions, we have estimated the pressure necessary to force the He stoichiometrically into the vacant sites of Si as few hundred Kbar, assuming a fixed lattice constant. One can envisage an ingenious pressure experiment so as to put a substantial amount of He into Si. Ion implantation of He, preferably along the channelling directions of Si with low kinetic energies, could be explored. Finally we may combine the effect of growing Si on substrate with a large lattice constant (in order to have large unit cells) with the latter method, to improve the way for producing HeSiSiHe.

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