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Ordered silicon–tin structures on a silicon (111) substrate

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Abstract. A structure for ordered silicon–tin systems on a silicon substrate, based on the known structure of a monolayer of tin on the (111) face of silicon, is proposed. The corresponding electronic structure of this system is modelled using the local density approximation to the density functional theory of the electron gas in the Kohn–Sham formulation with *ab initio* pseudopotentials taken for the electron–ion interaction. The total energy is minimized including relaxation of *all* the ionic positions, and the single electron states then evaluated. It is found that the overall energy gap in the band structure decreases rapidly with increasing tin concentration, and the direct gap is only 0.6 eV larger than the indirect gap for a tin concentration of 0.17 (a silicon concentration of 0.83). Effective masses of the electrons and the holes are evaluated at a tin concentration of 0.17. The lighter holes and electrons are found to be of similar mass to those in silicon. However, heavy electrons and holes are also found in the layer structure.

1. Introduction

There is much interest in the possibility of fabricating new semiconducting alloys and heterostructures with potentially advantageous device properties leading to applications that might be superior to those currently achieved using pure semiconductors (such as silicon and germanium) or compound semiconductors (such as gallium arsenide). Considerable effort has recently been expended in the study of the properties of Si/Ge superlattices [1–32] and also Si/Ge random alloys [33–49]. Some progress towards improved performance has been made with these systems (see, for example, [50]). But since silicon and germanium are rather similar electronically, it may be possible to advance even further towards this goal by using tin as an alloy constituent, given its small band gap in the semiconducting phase (0.082 eV) [51]. Investigations have already been made on germanium–tin systems, and specifically the equation of state for the α-phase of the tin–germanium alloy has been calculated [52]. Tight-binding calculations in the virtual crystal approximation [53] also show that the fundamental band gap (at low temperatures) can be varied from 0.76 eV down to 0.0 eV as the tin concentration is increased from zero to unity. Further, it is also observed that the gap passes from indirect (Γ–L) to direct (Γ–Γ) at a concentration of about 20% tin. If x is the fraction of germanium in the alloy, it appears that the alloy is actually a semi-metal for $x < 0.4$, a semiconductor with a direct gap for $0.4 < x < 0.8$, and then an indirect band gap semiconductor for $0.8 < x < 1.0$. Finally an experiment has recently been performed [54] in which a tin–germanium heterostructure is grown

(with two layers of tin and twenty layers of germanium for each section of the heterostructure) and which clearly demonstrates that heterostructures can be fabricated in a practical sense, provided necessary precautions are taken.

However, it is often desirable to use silicon as the major part of an alloy (as opposed to, for instance, germanium) since silicon very readily forms good oxide layers. Thus it is of particular interest to investigate the possibility that tin can be combined with silicon in order to produce other semiconductors with narrow band gaps which might subsequently be used to produce optimal infrared detectors, or narrow band gaps in the base of bipolar transistors, or in other applications. This is the primary motivation behind the work reported below, which is carried out within the local density approximation of density functional theory. It is recognized that such procedures generally underestimate band gaps; nevertheless we will show that silicon–tin systems are favourable candidates for systems with low band gaps.

2. Producing a silicon–tin structure

Tin and silicon have such different lattice constants (6.49 Å for semiconducting tin [55], versus 5.43 Å for silicon [56]) that they cannot form simple strained-layer heterostructures as do silicon and germanium. Moreover, since tin and silicon are thermodynamically insoluble [57] an attempt to form an alloy by bulk mixing will normally fail. However, a number of theoretical [58, 59] and experimental [60, 61] investigations of the properties of tin on the surface of silicon have been recently made from which it can be inferred that tin certainly does bond to a (111) surface of silicon, and does so in the structure shown in figure 1. The present investigation starts with this observation, and a heterostructure is imagined to be produced by depositing silicon after a tin layer, first filling in the sites between the tin atoms, and then forming one (or more) layers of pure silicon on top. More tin can then be laid down upon the silicon, and the process repeated until the desired thickness is reached.

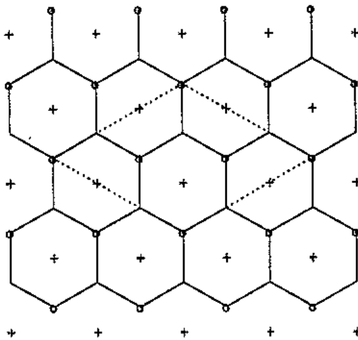

Figure 1. The arrangement of tin on the (111) face of silicon. The tin atoms lie at the corners of a rhombic unit cell.

Given this as a possible prescription for producing a silicon–tin system, it is necessary to compute the total energy of the system and the Feynman–Hellmann forces on the ions, to ascertain the stability of the system. Once this is done, the electronic properties can then be investigated. In this work, the corresponding calculations are performed using the local density approximation of density functional theory, with norm-conserving *ab initio* pseudopotentials [62]. A plane-wave basis is used, and the energy is minimized (including atomic relaxation) using the algorithm of Teter, Payne

and Allan [63]. Very briefly, the algorithm is as follows: the total energy functional is expressed in terms of a one-particle picture, and the one-particle wavefunctions are modified individually in the field of all the other wavefunctions using a preconditioned conjugate gradient method. At each step one wavefunction (and the corresponding contribution to the electron density) is updated in such a way as to maximize the reduction in the total energy. Large fluctuations of the charge density are avoided by this method of updating the wavefunctions since not only the first functional derivative of the energy with respect to the wavefunction being modified is used, but higher derivatives as well. This process is repeated for all occupied wavefunctions, and when all have been modified the procedure is begun again, and then repeated until the wavefunctions have converged. Ionic relaxation is performed as part of the total energy minimization, a step that is *crucial* to the ultimate aim of this paper. Once the ground state ionic positions and electron density are found, the electron energy bands are computed.

The first consideration for the calculations to be discussed below is the choice of unit cell. Three factors need to be included to define this. First the cell, when repeated periodically in three dimensions, must be able to reproduce the basic diamond structure. This is simply because tin is to be treated as a substitutional impurity in a silicon crystal (which has the diamond structure). Second, since the starting point for the formation of the system is the deposition of tin on the (111) face of silicon, it follows that when the cell is periodically repeated in two dimensions, the exposed face must be the (111) face. We observe that the face-centred cubic lattice (which underlies the diamond structure), when viewed as the stacking of spheres [56], has a (111) face exposed, and therefore has hexagonal symmetry. Third, the cell must have the correct shape and size to describe the unit cell for the tin atoms on the surface of the silicon. A $\sqrt{3} \times \sqrt{3}$ structure suitable for this calculation is shown in figure 1.

The rhombus described by the dotted line of figure 1 connects four of the sites at which the tin atoms are found to lie; this is chosen as the two-dimensional unit cell. Tin and silicon atoms are then positioned following the argument described above. The three-dimensional cell therefore contains a total of eighteen sites (see figure 2). One layer of tin corresponds to one site occupied by a tin atom in the cell; one layer of tin leads to a concentration of one tin atom for every seventeen silicon atoms.

Once the cell is established, a self-consistent calculation with relaxation of the ions is carried out using the algorithm of [63]. A plane-wave basis is taken with a cut-off energy of 14.0 Ryd, and three or four special k-points are used to calculate the electron density. The number actually depends on the symmetry of the cell; the density of points in the irreducible Brillouin zone is the same in each case. However, for the higher-symmetry system, the irreducible Brillouin zone is smaller than for the less symmetric case, so the number of points inside the irreducible zone is also correspondingly smaller. As might be anticipated it is found that only the nearest-neighbour silicon atoms tetrahedrally bonded to a tin that move by any significant amount (0.1–0.35 Å). The motion of the silicon ions during relaxation is always away from the tin, which may also be expected since the tin–silicon bond length (about 2.6 Å) is greater than the silicon–silicon bond length (2.35 Å). The procedure is then repeated for two, three and four tin atoms in the cell. For the case of two tin atoms (a concentration of one tin atom for eight silicon atoms), a pair of calculations is performed with the second tin atom being placed in one of two places. In the first, it is positioned so that the the two tin atoms are far enough apart that relaxation of silicon atoms around one tin atom can be taken as independent of that around

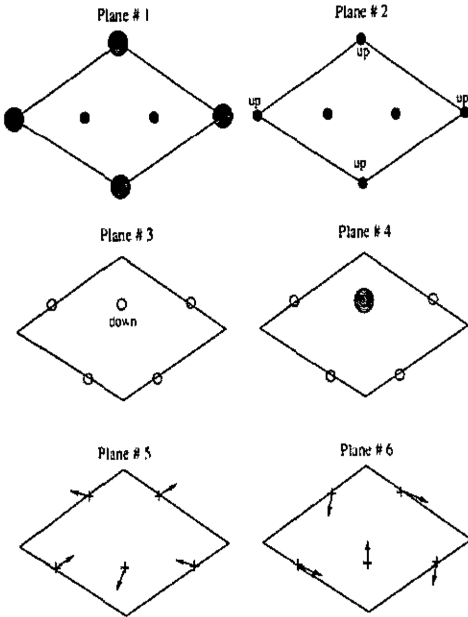

Figure 2. The atomic displacements for two tin atoms per unit cell. The tin atoms are marked by the large gray shaded circles. The arrows indicate the approximate direction of motion of the ions. Here 'up' and 'down' indicate that the atom moved out of or into the plane respectively.

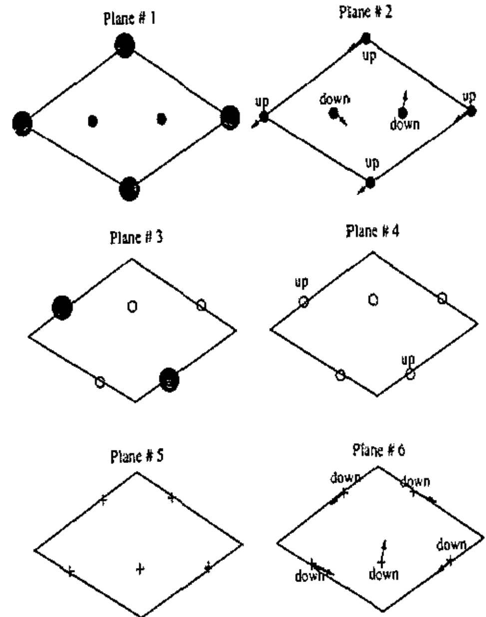

Figure 3. The atomic displacements for the alternative arrangement for two tin atoms per unit cell. The tin atoms are marked by the large gray shaded circles. The arrows indicate the approximate direction of motion of the ions. The words 'up' and 'down' indicate that the atom moved out of or into the page respectively. Where an arrow and a word appear on the same atom, there was motion both in the plane of the paper and perpendicular to the plane.

the other (two planes of silicon atoms between the planes containing the tin atoms). For the second, only one plane of silicon atoms is placed between the two planes containing tin. The maximum atomic displacements are larger in the latter case than in the former. (See figures 2 and 3. Note that these only show the general direction of motion, not the absolute values. Tables 1 and 2 give the exact displacements.) For the cases of three and four tin atoms per cell the separation between tin atoms is made as large as possible, though complete isolation is no longer possible. As noted, for each of these possibilities, complete atomic relaxation of all atoms is carried out, and only then are the energy bands calculated.

3. Results

It is interesting to plot the resulting band gap as a function of tin concentration for these fully relaxed structures; see figure 4. There appears to be a reasonably good linear relationship, though the gap at two tin atoms seems to depart somewhat from complete linearity (the dotted line is a linear interpolation between the gaps for one tin atom and three). The evident reduction in the size of the band gap with tin concentration can be mostly traced to the increase in the splitting between the two lowest conduction bands at the X point (in FCC notation), though when there are

Table 1. Atomic displacements for two tin atoms per unit cell, with the two tin atoms well separated.

x/a_0	y/a_0	z/a_0	$\delta x/a_0$	$\delta y/a_0$	$\delta z/a_0$	Atom type
0.000	0.000	4.488	−0.014	0.024	0.218	Si
2.094	3.628	5.984	0.001	0.024	0.061	Si
2.094	3.628	10.472	−0.007	−0.028	0.002	Si
4.189	7.255	11.968	−0.286	−0.031	0.057	Si
4.189	7.255	16.456	−0.156	−0.234	−0.065	Si
4.189	0.000	11.968	0.170	0.232	0.057	Si
4.189	0.000	16.456	0.281	0.018	−0.065	Si
6.283	3.628	0.000	−0.004	0.005	0.013	Si
6.283	3.628	4.488	−0.026	−0.038	−0.044	Si
8.378	7.255	5.984	0.014	−0.025	−0.252	Si
8.378	0.000	5.984	−0.022	0.011	0.061	Si
8.378	0.000	10.472	0.028	−0.008	0.002	Si
10.472	3.628	11.968	0.108	−0.187	0.076	Si
10.472	3.628	16.456	−0.118	0.204	−0.055	Si
12.567	7.255	0.000	−0.002	0.006	0.013	Si
12.567	7.255	4.488	0.046	0.003	−0.044	Si
0.000	0.000	0.000	0.001	−0.002	−0.002	Sn
8.378	7.255	10.472	−0.009	0.016	−0.034	Sn

Table 2. Atomic displacements for the alternative arrangement for two tin atoms per unit cell in which the tin atoms are not completely isolated from one another.

x/a_0	y/a_0	z/a_0	$\delta x/a_0$	$\delta y/a_0$	$\delta z/a_0$	Atom type
0.000	0.000	4.488	−0.143	−0.261	0.186	Si
2.094	3.628	10.472	0.011	−0.008	0.270	Si
4.189	7.255	16.456	−0.121	−0.212	−0.117	Si
4.189	7.255	11.968	−0.004	0.021	−0.010	Si
4.189	0.000	16.456	0.277	−0.015	−0.079	Si
6.283	3.628	0.000	0.019	0.026	−0.044	Si
6.283	3.628	4.488	0.266	0.005	−0.117	Si
8.378	7.255	5.984	0.038	−0.031	0.058	Si
8.378	7.255	10.472	0.008	−0.012	0.002	Si
8.378	0.000	10.472	−0.016	0.006	−0.014	Si
10.472	3.628	11.968	−0.034	0.021	0.002	Si
10.472	3.628	16.456	−0.145	0.241	−0.107	Si
12.567	7.255	0.000	−0.004	0.011	−0.029	Si
12.567	7.255	4.488	−0.122	0.219	−0.107	Si
4.189	0.000	11.968	0.036	−0.026	0.025	Si
8.378	0.000	5.984	−0.065	0.013	0.051	Si
2.094	3.628	5.984	0.015	0.004	0.054	Sn
0.000	0.000	0.000	−0.014	−0.001	−0.029	Sn

four tin atoms present per cell, the splitting at the top of the valence bands at Γ also makes a significant contribution; in turn this can be attributed to the increases in atomic diplacements. The gaps for the two cases discussed above with two tin atoms per unit cell are seen to differ from one another. The structure in which the two tin atoms are closer together has the smaller gap because of a splitting at the top of the valence bands at Γ (see figure 5) that is absent in the other case.

It would appear that for four tin atoms in the cell there is band overlap for

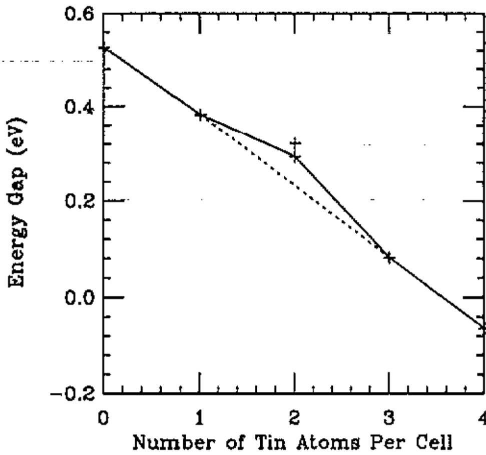

Figure 4. The overall energy gap versus tin concentration. Note that no correction has been made for the underestimate of the band gap by the LDA (known to be about 0.7 eV for silicon). The two points at a concentration of two tin atoms per unit cell correspond to two geometries at this concentration.

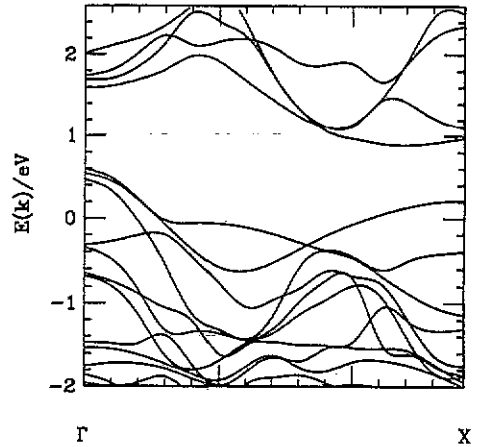

Figure 5. The band structure for the alternative arrangement of two tin atoms in the unit cell from Γ to X in the neighbourhood of the gap region.

the relaxed structure, making the system metallic. However, the correction to the band gap, made necessary by the consistent underestimate of the LDA, has not been included, and if it were included, we would expect to find that the system remains semiconducting. The band gap correction is known to be about 0.7 eV for silicon [64], but is expected to scale with the gap itself. Unfortunately, the precise variation cannot be found without more detailed many-body calculations. Finally it is noted that the bottom of the conduction band moves from Δ for zero, one and two tin atoms per cell, to X for three and four tin atoms (compare figures 5 and 6).

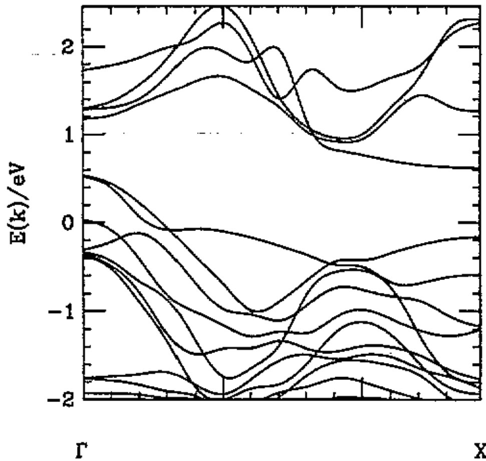

Figure 6. The bandstructure for three tin atoms in the unit cell from Γ to X in the neighborhood of the gap region.

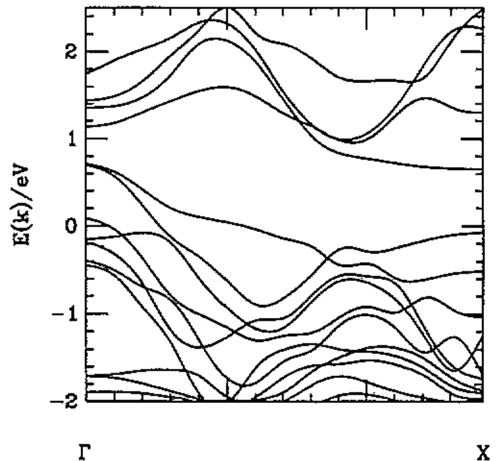

Figure 7. The bandstructure for four tin atoms in the unit cell from Γ to X in the neighborhood of the gap region.

Effective masses have been calculated for Sn_3Si_{15}. For the holes they are: 1.379, 0.344 and 0.380, and for the electron states they are: 0.129, 2.344 and 1.120. These are to be compared with the values for the silicon, where the holes have masses of 0.49 and 0.16, and the electrons have masses of 0.98 and 0.19 [65]. Heavy electrons are found because, in the folded structure, the bands are remarkably flat near X, which in turn is attributed to the opening up of the splitting between the two lowest conduction bands at X. The lowest conduction band undergoes a much larger change here than it does closer to Γ, and so the minimum at Δ is levelled out.

4. Discussion

The possibility of growing an ordered silicon–tin system by addition of tin to the (111) surface of silicon is found to lead to a corrsponding electronic structure with greatly reduced band gap as compared with silicon, even though the system contains mostly silicon. The resulting ordered system is found to be stable in a practical sense, provided large-scale atomic motion is prohibited (as would occur at a sufficiently high temperature, and which might lead to thermodynamic de-mixing). However, for the unit cells chosen, the minimum band gap is still indirect (the smallest direct gap is about 0.6 eV larger than the indirect one for three tin atoms in the unit cell, which is to be compared the difference of about 2.0 eV in silicon). These silicon ions tetrahedrally bonded to the tin ions are found to move away from the tin to allow for the increase in silicon–tin bond length as compared with the silicon–silicon bond length. There are found to be heavy electrons because of flattening at the bottom of the conduction band. The remaining question is primarily an experimental one, namely, whether or not the systems can be fabricated in practice. Success with this system would mean that it might be profitable to extend this type of investigation to other ordered heterostructures.

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