Surface Science 267 (1992) 83–86
North-Holland

surface science

Electronic structure and optical properties of short-period α-Sn_nGe_m superlattices

P. Vogl, J. Olajos [1], W. Wegscheider and G. Abstreiter
Walter Schottky Institut and Physik Department, Technische Universität München, W-8046 Garching, Germany

Received 7 June 1991; accepted for publication 1 July 1991

Short period α-Sn/Ge strained layer superlattices have been prepared on Ge(001) substrates by low temperature molecular beam epitaxy. We have achieved almost defect free and thermally stable single crystalline structures. Photocurrent measurements in a series of Sn_1Ge_m ($m > 10$) superlattices reveal a shift of the fundamental energy gap to smaller energies with decreasing Ge layer thickness m, in good agreement with band structure calculations. A direct fundamental energy gap and large direct band gap absorption is predicted for a slightly increased lateral lattice constant in α-Sn/Ge superlattices.

Band structure engineering is one of the most fascinating aspects of modern semiconductor physics. The easiest way to change artificially the electronic structure of semiconductors is the formation of semiconductor alloys. This, however, leads to potential fluctuations due to the random occupation of lattice sites by different atoms. Alternatively, new man-made semiconductors with tailored band gaps may be achieved with short-period superlattices. In the present communication we demonstrate that pseudomorphic, lattice matched short-period strained layer Sn/Ge superlattices (SLS's) can be realized experimentally and open the unique possibility to vary the energy gap in a wide range and even obtain a direct narrow gap semiconductor. We present detailed calculations and predict that these α-Sn_nGe_m SLS's can have intrinsically direct energy gaps at $k = 0$ for certain strain conditions *which are not caused by a folding of electronic states into the superlattice Brillouin zone* and lead to a strong band edge interband absorption. In addition, we report on the experimental realization of almost defect free and stable α-Sn_nGe_m superlattices which have been grown by low-temperature molecular beam epitaxy (MBE) on Ge(001) substrates.

Recently, several groups tried to grow α-Sn or α-Sn_xGe_{1-x} alloys by heteroepitaxy on various substrates [1–6]. The phase transition of Sn from the diamond structure α-phase to the metallic body centered tetragonal β-phase at $T = 13.2\,^\circ C$ causes Sn to be a difficult material to deal with. We have used a new and unconventional technique to grow high quality α-Sn/Ge superlattices [7]. The multilayer structures were deposited in a special MBE system which allows strong temperature variations during growth. The layers were deposited far away from thermodynamic equilibrium conditions with a substrate temperature modulation between about 50 and 300 °C during growth. Details of growth properties and growth conditions have been published elsewhere [7]. A series of samples have been prepared under optimized conditions. They consist of 20 periods of Sn_1Ge_m ($m = 11$, 15 and 21) superlattices which have been grown on Ge(001) and repeated four times with 700 Å Ge layers in between. From detailed in-situ Auger analysis and post-growth characterization by Raman spectroscopy and high

[1] Permanent address: Dept. of Solid State Physics, University of Lund, S-221 00 Lund, Sweden.

resolution TEM, we could extract a concentration profile of the superlattices. The concentration of Sn in the first atomic plane turns out to be approximately one third of a monolayer, followed by an exponential decay and a negligible Sn content beyond a coverage of ten monolayers Ge.

In order to get information on the fundamental band gap of these (SnGe)/Ge superlattices, we have performed infrared photocurrent measurements. Ohmic contacts were obtained by evaporating Ti/Sb/Au on the rectangular shaped cleaved samples and annealing for 30 s at $T = 320\,^{\circ}C$. Care has been taken to avoid the α to β phase transition of the Sn or the SnGe alloys. We determined the critical temperatures to be $T_c = 430$, 450 and 465 °C for Sn_1Ge_{11}, Sn_1Ge_{15} and Sn_1Ge_{21}, respectively. Photocurrent measurements were performed in the energy range 0.4 to 1.1 eV using a quartz halogen light source together with a single grating monochromator and filters. The samples were mounted in a He cryostat. The transmittance of the whole system was calibrated with a pyroelectric detector such that the measured photocurrent could be normalized to the incident photon flux. The samples were cooled to liquid He temperatures in order to freeze out the holes in the epitaxial Ge layers which turned out to be unintentionally boron doped due to the boron nitride crucibles used in our low temperature MBE system. In addition to the superlattice samples, we also measured the photocurrent of a Ge reference sample which was grown under the same conditions.

In the Ge reference sample, we observed a large photocurrent above 0.75 eV due to interband electron–hole excitations. The photocurrent spectra of the superlattices exhibited, in addition, a strong signal below the Ge band gap whose onset is clearly shifted to smaller energies with decreasing Ge concentration. Fig. 1 shows the relative change of the absorption coefficient α versus energy for three superlattice samples. The absorption edge is rather smooth and shifts roughly from 0.66 eV for Sn_1Ge_{21} to 0.56 eV for Sn_1Ge_{11}. The arrows underneath each of the experimental curves in fig. 1 mark the theoretically predicted energy gaps, as obtained from superlattice band structure calculations which are discussed below. In particular, the black arrows correspond to the calculated fundamental energy gap for perfectly sharp SLS's. It is indirect in k-space. The grey arrows mark the predicted energy gaps of smeared out concentration profiles. The actual samples have a compositional profile somewhere in between these two extreme cases. The positions of the absorption edges and their shift with the Ge content are in very good agreement with the calculated energy gaps.

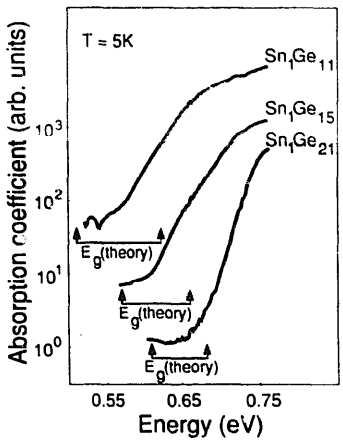

Fig. 1. Absorption coefficient below 0.75 eV as extracted from the normalized photocurrent data. The black and grey arrows mark the theoretically predicted indirect energy gap of the strained layer superlattices with sharp interfaces (no intermixing of Sn and Ge) and smeared out Sn-profiles, respectively.

The present calculations indicate that the electronic structure of α-Sn_nGe_m SLS's is controlled by a unique interplay between very large strain effects, spin–orbit interaction effects, as well as quantum confinement of electronic states. Since the α-Sn_nGe_m SLS's are grown pseudomorphically on Ge(001), the Sn layers have a lateral lattice constant $a_{\parallel} = a_{Ge} = 5.65$ Å. This compression corresponds to a lateral strain of approximately 13% in the Sn layers. For tetragonally distorted pure α-Sn layers, we obtain a lattice constant normal to the planes $a_{\perp} = 7.204$ Å from macroscopic elasticity theory. We have calculated the electronic structure of α-Sn/Ge superlattices employing the empirical, nonlocal relativistic pseudopotential method of Chelikowski and Cohen [8] and generalizing it to superlattices. This generalization amounts to a smooth interpolation and volume renormalization of the bulk pseu-

dopotential form factors for the simple tetragonal supercell and introduces no additional parameters. We have extensively tested our calculations by applying it to Ge_nSi_m SLS's. Our results compare very well with the gap-adjusted LDA calculations of [9,10].

Unstrained bulk diamond-type α-Sn ($a = 6.498$ Å) is known to have a zero-gap at $k = 0$ [11]. The present pseudopotential calculations predict that (001)-biaxially compressed (i.e. tetragonal) α-Sn with $a_{\parallel} = a_{Ge}$ has a metallic ground state. Whereas the (001)-strain opens a gap at $k = 0$, the conduction bands at N (corresponding to L in the diamond structure) are shifted downwards to an energy of -0.4 eV below the Fermi energy. To summarize, we find that a single heterostructure consisting of a half-infinite Ge crystal and a laterally lattice matched half-infinite α-Sn crystal is metallic and has no energy gap.

The situation changes dramatically in a short-period superlattice with $a_{\parallel} = a_{Ge}$ and very few Sn layers. The quantum-mechanical confinement of the electronic states in the ultra-thin Sn-layers of the superlattice causes the Sn-related conduction bands at $N(L)$ and Γ to raise above the Ge-related conduction band edge states. Consequently, there is a positive gap in the series of short-period SLS's α-Sn_nGe_m with $n < m/2$. Importantly, the lowest conduction band edge states for these SLS's are Ge-derived anti-bonding states which are strongly confined to the Ge layers; in addition, the energy gap is principally smaller than in pure Ge. The latter finding originates in the Sn–Ge bond being weaker than the Ge–Ge bond; accordingly, the bonding–antibonding splitting in a SnGe compound is smaller than in pure Ge.

To compare with our experimental data, we have performed detailed calculations of α-Sn_1Ge_n superlattices with $n = 3, 7, 11, 15, 19$ on Ge substrate, i.e. with $a_{\parallel} = a_{Ge}$. In all of these cases, we find the top of the valence band at Γ, and the bottom of the conduction band at L'. We note that the superlattice k-point L' corresponds to the L-point in the fcc structure and is equivalent to $k = X$ for an 8- or 16-period SLS and $k = R$ for a 4-, 12- or 20-period SLS (see Fig. 2b). This indirect band gap increases with increasing n but approaches the value of bulk Ge very slowly. Fig. 2 shows the calculated band structure of an α-Sn_2Ge_6 SLS. The superlattice Brillouin zone is also shown as inset in fig. 2b. To account for the interface mixing, we have also calculated the electronic structure of smeared out Sn profiles, employing the virtual crystal approximation. The calculations predict a small increase of the energy gap with intermixing, as indicated in Fig. 1 with the black and grey arrows, respectively.

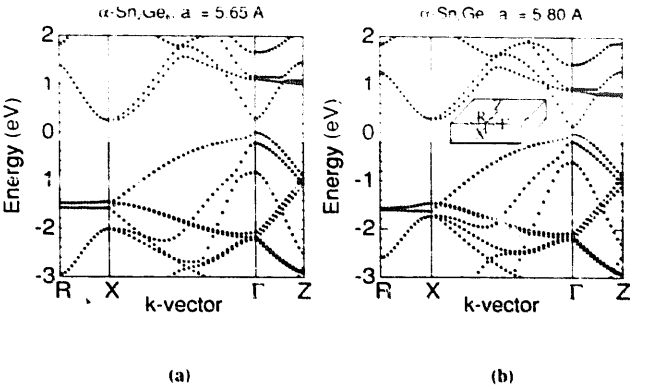

Fig. 2. Calculated band structure of an α-Sn_2Ge_6 superlattice with a lateral lattice constant $a_{\parallel} = 5.65$ Å (a) and an α-Sn_2Ge_6 superlattice with $a_{\parallel} = 5.80$ Å (b). The superlattice Brillouin zone is shown schematically as inset in (b).

According to the present theory it is also possible to produce a direct energy gap in α-Sn_nGe_m SLS's with strong interband optical transition matrix elements just by slightly increasing the lateral lattice constant. A lateral lattice constant larger than a_{Ge} leads to a biaxial expansion – and consequently also to a hydrostatic expansion – of the Ge layers. Analogously to most semiconductors, this yields a decrease of all conduction bands, with a decrease at $k = \Gamma$ which is three times larger than at $k = L'$. Since the superlattice conduction and valence band edge states are almost purely Ge-like, a slight increase of $a_{\parallel}$ already produces a direct energy gap at $k = 0$ for a wide range of α-Sn_nGe_m SLS's with $n < m/2$. The α-Sn_2Ge_{10} superlattice, for example, is direct for 5.7 Å $< a_{\parallel} <$ 6.0 Å. Another example is shown in fig. 2b for the case α-Sn_2Ge_6 and $a_{\parallel} = 5.80$ Å. Since the band edge states are Ge-like states, this figure shows effectively the conversion of Ge, embedded in a SLS with a few Sn layers, into a crystal with an InSb-like band structure.

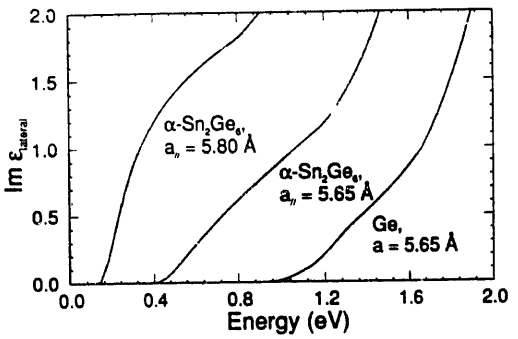

Fig. 3. Calculated imaginary part of the lateral matrix element of the dielectric tensor as a function of energy for α-Sn_2Ge_6 superlattices and pure Ge.

In order to investigate the optical properties of α-Sn$_n$Ge$_m$ SLS's, we have calculated the imaginary part of the optical dielectric function $\epsilon(\omega)$ in the random phase approximation,

$$\mathrm{Im}\,\epsilon_{ij} = \frac{4\pi^2 e^2 \hbar^2}{m^2 \omega^2 V} \times \sum_{n}^{\mathrm{occ}} \sum_{n'}^{\mathrm{unocc}} \sum_{k} \langle nk | \nabla_i | n'k \rangle \langle n'k | \nabla_j | nk \rangle \times \delta(\hbar\omega - (E_{n'k} - E_{nk})).$$

Here, i and j denote the components along the crystal axis, ω is the frequency, m and e are the electronic charge and bare mass, V is the crystal volume, and $|nk\rangle$ denote the SLS's Bloch states as obtained from the pseudopotential calculations. The tetragonal symmetry gives two different diagonal matrix elements, $\epsilon_{11} = \epsilon_{22} = \epsilon_{\parallel}(\omega)$ and $\epsilon_{33} = \epsilon_{\perp}(\omega)$. The difference between these matrix elements, however, is not significant in the α-Sn$_n$Ge$_m$ SLS's we have investigated. In fig. 3 we show the calculated Im $\epsilon_{\parallel}(\omega)$ near the band edges for pure Ge, Ge-lattice matched α-Sn_2Ge_6 ($a_\parallel$ = 5.65 Å), and laterally relaxed α-Sn_2Ge_6 ($a_\parallel$ = 5.80 Å), respectively. The latter SLS has a strikingly large direct dipole-allowed band gap transition rate. In fact, even α-Sn_2Ge_6 on Ge-substrate already has a much larger band edge transition rate than pure Ge, inspite of its borderline indirect nature. Thus, α-Sn$_n$Ge$_m$ SLS's appear to be promising candidates for converting crystalline, periodic group-IV structures to direct narrow gap semiconductors.

References

[1] R.F. Farrow, D.S. Robertson, G.M. Williams, A.G. Cullis, G.R. Jones, I.M. Young and P.N.J. Dennis, J. Cryst. Growth 54 (1981) 507.
[2] J.L. Reno and A.L. Stephenson, Appl. Phys. Lett. 54 (1989) 2207.
[3] M.T. Asom, A.R. Kortan, L.C. Kimerling and R.C. Farrow, Appl. Phys. Lett. 55 (1989) 1439.
[4] S.J. Shak, J.E. Greene, L.L. Abeles, Q. Yao and P.M. Raccah, J. Cryst. Grotwh 83 (1987) 3.
[5] R.P. Pukite, A. Harwit and S.S Iyer, Appl. Phys. Lett. 54 (1989) 2142.
[6] H. Höchst, M.A. Engelhard, and J. Hernández-Calderón, Phys. Rev. B 40 (1989) 9703.
[7] W. Wegscheider, K. Eberl, U. Menczigar and G. Abstreiter, Appl. Phys. Lett. 57 (1990) 875.
[8] J.R. Chelikowski and M.L. Cohen, Phys. Rev. B 14 (1976) 556.
[9] S. Saipathy, R.M. Martin and C.G. van de Walle, Phys. Rev. B 38 (1988) 13237.
[10] U. Schmid, N.E. Christensen, M. Alonani and M. Cardona, Phys. Rev. B, to be published.
[11] C.H.L Goodman, IEEE Proc. 129 (1982) 189.