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Superlattices Based on Group IV Elemental Semiconductors(Si, Ge, α-Sn)

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We report on recent results in the realization of direct energy-gap materials based on group IV superlattices: Si, Ge, and α-Sn.
Sn_nGe_m superlattices have been fabricated with an MBE method involving large temperature variations. A downward shift of the energy-gap of the superlattices with increasing α-Sn concentration is observed.
In the strain-adjusted Si_nGe_m superlattices, grown on step-graded $Si_{1-x}Ge_x$ alloy bufferlayers, an enhanced Photoluminescence and Electroluminescence is observed, wich can be attributed to interband transitions in the superlattices.

1. Introduction

The possibility of achieving a direct band-gap material based on the group IV semiconductor elements is a fascinating task that has attracted a great amount of interest and effort during the last years. Although theoretical predictions were done already some decades ago about increased oscillator strengths in structures where the cubic symmetry was artificially broken by the different constituent elements in superlattices, the realization of these 'new' materials has only been achieved recently due to the developement of growth techniques such as molecular beam epitaxy (MBE) which allow precise control of layer thicknesses on an atomic scale.

In the Si/Ge system a 'quasi-direct' band-gap was proposed both by simple 'zone-folding' type of arguments[1] as well as with more sofisticated theoretical considerations performed recently. Experimental evidence for enhanced oscillator strengths in these superlattices has, however, been lacking uptil only very recently [2] since the dislocation-densities were too high to allow unambiguous studies of the intrinsic optical properties.

For the α-Sn/Ge-system, a true direct and not 'quasi-direct' bandgap is proposed for certain conditions. However, the problems in the crystal-growth of these structures are even larger than for the Si/Ge system partly due to inherent properties of Sn as e.g phase-transition and segregation.

In this paper, experimental results will be presented which show that a significant step towards the realization of group-IV-based optelectronic materials has been taken and that the intrinsic optical properties of these materials now can be examined.

2. α-Sn_nGe_m superlattices

Alloys of $Ge_{1-x}Sn_x$ with diamond-structure are interesting materials due to their expected narrow direct bandgap and lack of polar phonon scattering [3]. As seen in Fig 1, a linear interpolation between the bulk band structures of α-Sn and Ge should yield a material with a fundamental direct energy-gap for Sn contents in the range of about 20% to 70 %. This is a consequence of the band ordering at **k**= 0 of the semimetallic α-Sn phase (grey tin).

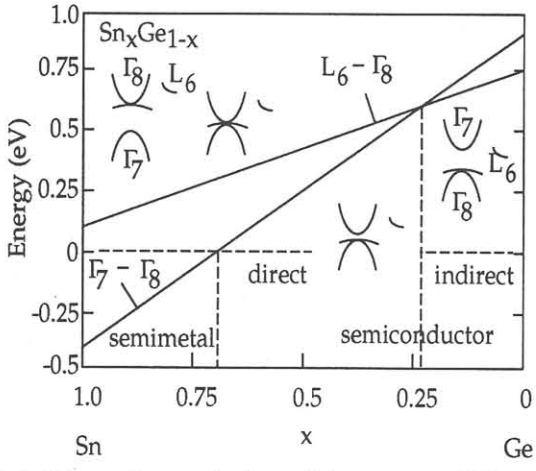

Fig1. Linear interpolation of the energy differences Γ_7-Γ_8 and L_6-Γ_8 between the bulk band structures of α-Sn and Ge

Although it is a very simple approximation that the energy positions at the critical points in the bandstructure should vary linearly with composition, the three band-gap types 'semimetallic, direct, and indirect' which are shown in Fig.1 are also expected from more elaborate theoretical calculations.

The difficulties in preparing α-Sn/Ge structures of high crystalline quality which make it possible to study bandgap energies are due to basic physical properties of Sn. It is e.g. well known that Sn undergoes a phase transition at 13.2° C to the metallic body-centered-tetragonal β- phase with a large reduction in volume. It is, however, possible to increase the transition temperature by growing thin films of α-Sn and $Ge_{1-x}Sn_x$ on substrates of different material e.g. InSb, GaAs and Ge. Other difficulties that must be overcome are the large lattice mismatch, the low solid solubility of the two elements in each other, and the strong tendency of Sn to segregate on Ge.

A new and unconventional growth technique far away from thermal equilibrium has been used recently[4] for the fabrication of high-quality α-Sn/Ge short-period superlattices. The method includes low-temperature MBE and large temperature variations during growth as can bee seen in Fig.2.

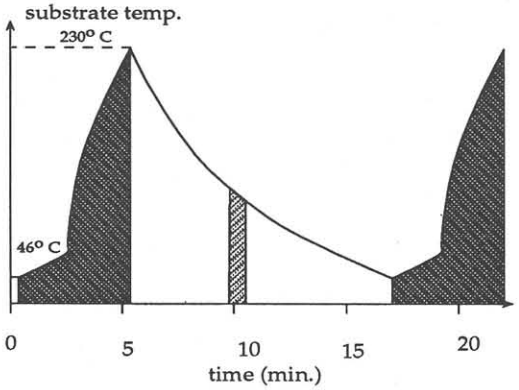

Fig.2 Growth temperature of a Sn_2Ge_{20} superlattice as a function of time. The hatched regions indicate the times when either the Ge or the Sn shutter was open.

High quality Sn_nGe_m superlattices have been achieved for $n \leq 2$ and $m \geq 10$ where n and m are the number of monolayers of Sn and Ge, respectively.

The fundamental energy gaps of a series of superlattices : Sn_1Ge_{11}, Sn_1Ge_{15}, and Sn_1Ge_{21} have been studied by means of photocurrent and direct absorption spectroscopy[5]. As expected, the band-gap shifts to lower energies with increasing Sn concentration. Absorption spectra are shown in Fig.3 together with a reference Ge- spectrum. A comparison of the experimentally determined bandgap energies, obtained with a fitting to the absorption curves to theoretiaclly calulated bandgap energies obtained with the non-local, empirical pseudopotential method generalized to superlattices, is shown in the inset in Fig.3. As can be

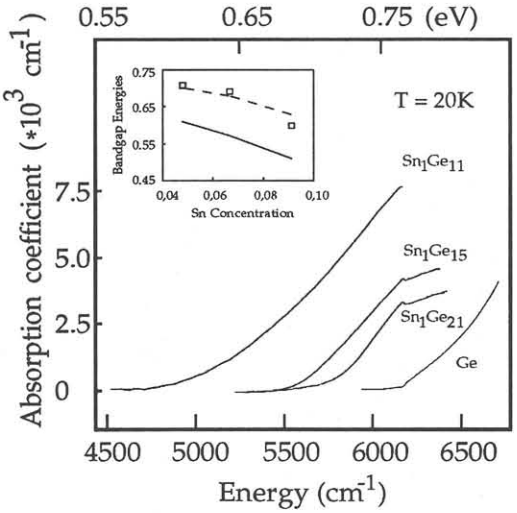

Fig.3 Absorption coefficient for the Sn_1Ge_m (m= 11,15,21) superlattices. In the inset, a comparison is shown between the experimental values (open sqares) and theoretical data obtained from ref.5

seen, an excellent agreement between the experimentally determined bandgap energies and theory is found when assuming a realistic smeared-out Sn concentration profiles. (broken lines).

3. Strain-symmetrized Si_mGe_n superlattices

The luminescence from Si/Ge short period, strained layer superlattices (SLS's) has also attracted considerable interest over the last years, but not until recently have there been samples available with good enough quality concerning dislocation densities, interface sharpness etc. such that reliable studies of the intrinsic optical properties could be performed in these structures. The breakthrough during the last years in the improvement of the PL properties of the Si_mGe_n SLS has been a result of the ability in reducing the dislocation density during growth. This is acomplished in several ways e.g. by growing the buffer with continously increasing Ge concentration [6], so called step-graded or linearly graded bufferlayers. A further improvement is achieved by using surfactants during growth.

In a recent paper[2] the PL properties of a series of strain-adjusted Si_mGe_n SLS were examined. An enhanced photo-luminescence was observed in the superlattices as compared to a Si/Ge alloy and arguments were given for a excitonic radiant recombination via localized excitons, bound to potential fluctuations in the superlattice. The PL spectra of these samples are shown in Fig.5. The random alloy sample exhibits two peaks at 0.985 and 0.929 eV which can be attributed to a no-phonon(NP) transition and an associated phonon replica

involving a transverse optical phonon respectively [7]. At lower energies, corresponding PL lines from the SLSs are observed. These signals shift to lower energies with increasing period length but ot-

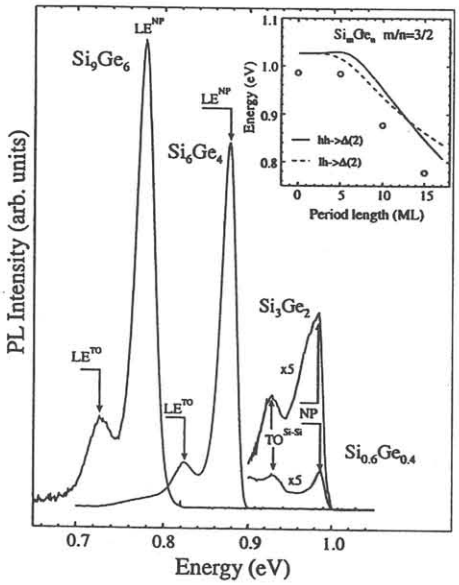

Fig. 4 PL spectra for Si_9Ge_6, Si_6Ge_4, and Si_3Ge_2 SLS and a $Si_{0.6}Ge_{0.4}$ alloy.

herwise identical Si/Ge ratio, in accordance with an effective-mass calculation shown in the inset. Taking into account that the SLS region is only about 300 nm thick, an enhancement of a factor of 150 is found for the PL intensity from the SLSs as compared with the random alloy. Furthermore, also the onset of band-to-band transitions were observed for all SLS samples in an energy region just above the corresponding NP-line. These measurements, together with other experiments as annealing and hydrostatic pressure-dependances of the luminescence lines gave further strength to the assignment of the PL as being (near-) bandgap luminescence.

Electroluminescence spectra as detected at room temperature from a Si_6Ge_4 SLS grown in a p^+n configuration has very recently been reported [8]. Such spectra at three different heat-sink temperatures: 159K, 218K and 296K, measured with the same injection current density (3 A/mm^2) are shown in Fig.3. It is seen that the signal consists of in principle two broad features with peak energies of 0.77 eV and 0.88 eV, respectively, and that the relative intensity of the two peaks are temperature dependent. A typical L-I plot, obtained with a heat-sink temperature of 156K, is shown in the inset of Fig. 5 where the intensity of the 0.77 eV and the 0.88 eV- peaks are marked with full and open circles, respectively. Several important observations are noteworthy from this graph, namely : (1) the intensity of both peaks shows a superlinear dependence for certain current densities, (2) the onset of superlinearity occurs at similar current densities for both peaks, and (3) the

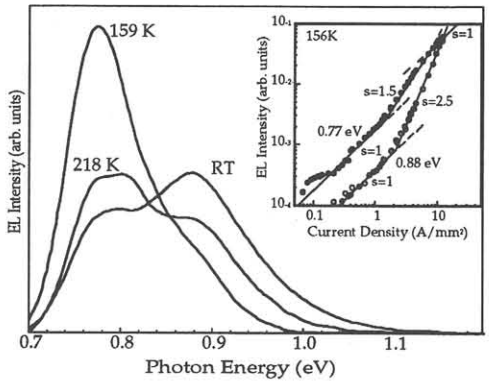

Fig.5 EL spectra measured at an injection current of 3 A/mm^2 at three heat sink temperatures. The inset shows the EL intensity measured at a heat sink temperature of 156K as afunction of injection current density for the two peaks.

slopes of the L-I lines are approximately equal to 1 before and after the superlinear region, at least for the 0.77 eV - peak. The superlinearity is characteristic of a multi-state model of recombination channels across and in the forbidden energy gap of the semiconductor[ref]. In our case, this means that the two observed EL peaks originate from the same region of the sample if they compete with the same non-radiative recombination channel. We believe that the high-energy peak originates from free-to-free interband transitions, whereas the low-energy peak is defect related.

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