Sensors & Transducers, Vol. 209, Issue 2, February 2017, pp. 28-34

Sensors & Transducers
Published by IFSA Publishing, S. L., 2017
http://www.sensorsportal.com

Study of GeSn Alloy for Low Cost Monolithic Mid Infrared Quantum Well Sensor

Prakash PAREEK and Mukul K. DAS
UGC SAP Research Laboratory, Department of Electronics Engineering
Indian Institute of Technology (Indian School of Mines) Dhanbad, Dhanbad-India
Tel.: +917549028379
E-mail: ppareek1@gmail.com

Received: 25 December 2016 /Accepted: 30 January 2017 /Published: 28 February 2017

Abstract: This paper focuses on theoretical study of Tin incorporated group IV alloys particularly GeSn and design of quantum well sensor for mid infrared sensing applications. Initially, the physics behind the selection of material for midinfrared sensor is explained. The importance of controlling strain in GeSn alloy is also explained. The physical background and motivation for incorporation of Tin(Sn) in Germanium is briefly narrated. Eigen energy states for different Sn concentrations are obtained for strain compensated quantum well in Γ valley conduction band (ΓCB), heavy hole (HH) band and light hole (LH) band by solving coupled Schrödinger and Poisson equations simultaneously. Sn concentration dependent absorption spectra for HH- ΓCB transition reveals that significant absorption observed in mid infrared range (3-5 µm). So, $Ge_{1-x} Sn_x$ quantum well can be used for mid infrared sensing applications.

Keywords: GeSn, Strain, Midinfrared, Quantum well, Tin incorporated group IV alloy.

1. Introduction

In last few years, mid infrared sensors (MIR) have drawn attention of researchers from all over the world due to their vast applications. They found their presence in defence, surveillance, medical, information security applications [1]. Group III-V based MIR have already proven their worth by showing excellent performance in past. However, III-V material like GaAs is too expensive for commercial uses. They are also incompatible to Silicon to realize a monolithic sensor. Thus, researchers compelled to look for a new class of material which can enable the design of low cost single chip mid infrared photosensitive devices. Both Silicon (Si) and Germanium (Ge) are two obvious choice to realize low cost MIR. This is due to their compatibility with microelectronics technology, and low cost which can made design of low cost single chip MIR feasible.

Unfortunately due to their indirect band gap nature both Si and Ge are not suitable to be used in active optoelectronic devices like MIR. So, it is necessary to employ some band engineering techniques in Si and Ge to induce direct band gap in them. Between these two, Germanium is the most appropriate material for implementation of band engineering due to the reason as follows. In Ge, the direct bandgap EΓ is only 140 meV larger than the indirect bandgap at L valley [2].

The most important approach of band structure engineering in Ge is incorporation of Tin (Sn) in the Germanium. With incorporation of small amount of Tin into Ge, L and Γ valley decreases. Decrement of Γ is faster than that of L valley and hence direct bandgap can be obtained at a particular value of mole fraction of Tin [3]. Thus GeSn alloy can enable the design of low cost group IV photonic sensors which are as efficient as their III-V group counterpart. However, due to larger lattice mismatch between Ge and Sn, strain plays a critical role in physics of GeSn alloy. So, it needs to be addressed in a proper manner. Strain balanced structures are suggested to be the best way to tackle excessive strain in multiple layer structure like Quantum well [4]. It not only protects the active layer from excessive strain but also provide an opportunity to maximize its thickness, which is a good thing for photosensitive devices.

This paper focuses on the potential of Tin doped group-IV alloys specially GeSn to be used as an active layer in photosensitive devices like detector. It is the extension of our work reported elsewhere which highlighted potential of Tin incorporated quantum well application as a sensor in brief [5]. Here we give a detailed physical background of Tin incorporated group IV alloy. It highlights the recent progress and challenges in the research and fabrication of these alloys. This work primarily focuses on the use of these alloys in photo detectors. Absorption coefficient is a significant performance parameter in these devices. In this study, Sn content dependent absorption coefficient is evaluated in strain balanced SiGeSn/GeSn strain balanced quantum well. Eigen energy states for different Sn contents in GeSn layer are obtained in the well for Γ valley conduction band (ΓCB), heavy hole (HH) band and light hole (LH) band separately by solving coupled Schrödinger and Poisson equations self consistently. The absorption characteristics are evaluated for different Sn contents in well. The result revealed that HH-ΓCB transition observes high absorption coefficient within 3-5 μm range of wavelength. Thus this well structure can be used as an infrared sensor in various applications.

2. Tin Incorporated Group IV Alloy-Physical Background and Brief Review

Tin, the element that lies below germanium in the periodic table, can crystallize in the diamond structure (α-Sn) as well as in its more familiar metallic form (α-Sn). Only relatively poor specimens of this grey α-Sn had been prepared, however, as it is only formed rather slowly from metallic tin and at temperatures below 13 °C. (and retransforms back to α-Sn above that critical transformation temperature) [6]. The best specimens of α-Sn were in fact obtained by recrystallizing from solution in mercury [7], but such material probably was never of very high crystal perfection, although it could apparently be prepared in relatively pure form (about 10^{15} donors/cm3). The pioneer of inducing the idea of Tin based direct band gap semiconductor was Prof. Goodman who on the basis of theoretical grounds and substrate stabilization effect proved that an alloy of α-Sn and Ge solution can show a directness in its bandgap [6]. Soref and Perry have predicted the direct band gap of Sn based group IV semiconductor (SiGeSn) in year 1991 [8].

$Ge_{1-x}Sn_x$ alloys have attracted a great deal of interest in recent years due to their potential to become the first group IV direct band gap alloys. Diamond cubic Sn (or α-Sn) is a semimetal with a conduction band minimum at the Γ point sitting 0.41 eV below the valence band [9]. By alloying Sn and Ge, the conduction band extrema at both L and Γ valleys are predicted to decrease in energy with increasing Sn composition, but the Γ valley is predicted to decrease more rapidly than the L valley. Tight-binding [9] and pseudopotential [10] electronic structure calculations in virtual crystal approximation predict that $Ge_{1-x}Sn_x$ alloys would undergo an indirect to direct transition with a continuously tunable direct energy bandgap from 0.55eV to 0eV for Sn composition of x=0.2 to 0.6. Due to some difficulties in growing GeSn, Energy bandgap and Sn composition relation was not published until 1997 in which the indirect to direct band gap transition was estimated to occur near x=0.1 which is much lower than the theoretical prediction [11]. The critical concentration for the crossover for germanium for transition from indirect to direct was found as x=0.11 for relaxed Ge1-xSnx [12]. For different composition ratios, this alloy can be divided into two main branches first one is α- Sn film with Ge doping (dilute GeSn alloy) which has been reported by Farrow et. al. in 1981 [7], Goodman in 1982 [6], Vnuk et. al. in 1983 [13] and Ge rich Ge_{1-x} Sn_x alloy was reported by [14-16]. Already in the 1980s and 1990s, several groups were studying the fabrication of α-Sn [17-19] or GeSn alloys [14, 20-22]. However several challenges for the single crystalline growth of GeSn alloys were found. Ragan et. al. [16] had given several problems that hindered the utilization of GeSn alloy. They highlighted the three main challenges to overcome:

(i) Minor solid solubility of Sn in Ge < 0.5 %

(ii) A large lattice mismatch between Ge and Sn (~15 %)

(iii) Sn has low surface free energy which causes surface segregation.

All investigations from the 1980s and 1990s showed that growth conditions far away from the thermodynamic equilibrium have a chance to produce monocrystalline GeSn alloys. $Ge_{1-x}Sn_x$ alloys with x<0.2 (x=mole fraction of tin) had been grown on silicon by ultrahigh vacuum chemical vapour deposition. By experimental investigation it had been proved that significant changes occurs in optical constants and redshifts in the interband transition energy as x varied [23, 24]. Suyog Gupta et. al. [25] addressed the challenges mentioned above and presented a first principles based simulation method to estimate lattice and electronic properties of GeSn alloy. They used low temperature molecular beam epitaxy (MBE) to obtain high quality crystalline GeSn layers. Modern semiconductor technology requires epitaxial layers with a prescribed band gap and lattice constant. This dual requirement cannot be implemented via 'one dimensional' binary A_xB_{1-x} or pseudo binary $A_xB_{1-x}C$ alloys. So it has motivated the quest for 'two-dimensional' ternary ($A_xB_yC_{1-x-y}$), pseudo-ternary ($A_xB_yC_{1-x-y}$ D), or quaternary

($A_xB_{1-x}C_yD_{1-y}$) materials whose band gaps and lattice constants can be tuned independently [26, 27].

Group III –V quaternary semiconductors were so successful in decoupling strain and band structure effects gave an impression that ternary group IV semiconductor such as SiGeC and SiGeSn should play similar role in group IV regime. SiGeC was reviewed at least for a decade and it was find out that only a limited amount of carbon can be incorporated and carbon induces a perturbation that make the band structure explanation extremely difficult even by virtual crystal approximation method [28, 29]. Tensile strain on Ge can be produced by growing this material on relaxed $Ge_{1-x}Sn_x$ as reported by Soref and Friedman [30]. However the direct bandgap (Γ valley) of $Ge_{1-x}Sn_x$ decreases very rapidly as a function of x. The solution to this problem is the incorporation of Si, which raises the energy of the alloy band gap. Si also reduces tensile strain on the Ge layer but a compromise can be achieved in such a way that the direct bandgap in Ge is also the lowest band gap in $Ge/Ge_{1-x-y}Si_xSn_y$ multilayer [31]. Advances in CVD growth technology [32, 33] propels work in SiGeSn horizon.

Thus several studies have carried out for fabrication of high quality GeSn layers but the role of strain should be considered. Therefore, strain balanced structure is becoming very vital. In next section strain compensated structure and its used in implementation of photosensitive device is highlighted in brief.

3. GeSn MIR Sensor

3.1. Model Description

The Quantum well structure considered in our analysis consists of tensile strained SiGeSn barriers and compressively strained GeSn well which ensures the strain balanced condition for quantum well. The growth axis of the structure is assumed along (001) axis. A 76Å thick $Ge_x\,Sn_{1-x}$ layer is sandwiched between two tensile strained $Si_{0.09}\,Ge_{0.8}\,Sn_{0.11}$ layers to form a type-I single quantum-well (SQW) as shown in Fig. 1.

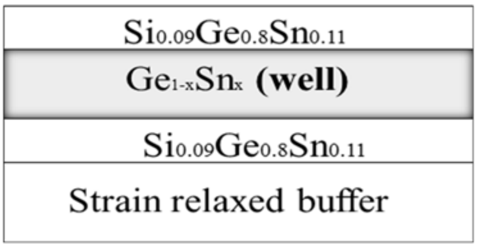


Fig. 1. Schematic of Strain balanced GeSn/SiGeSn Quantum well.

The thickness of barrier is computed as 35 Å by using strain compensate condition [4]. The dimension of the well is chosen in such a way that only one bound state formed in each of the conduction band and valence band. The Sn composition (x) in QW is required to obtain three condition simultaneously, (i) Type I SiGeSn/GeSn quantum well for better quantum carrier confinement, (ii) direct band gap in GeSn layer and (iii) a higher value of HH band offset than that of LH band (to be calculated later) for TE mode operation, which features HH-ΓCB dominant transition. A fully relaxed GeSn layer is used as a buffer layer. The composition of buffer layer should be selected to maintain strain balanced condition in the QW.

3.2. Band Alignment Calculations

Accurate band profile and band discontinuities of the proposed QW structure is the vital requirement for precise modeling of the direct band interband absorption. The strain plays an important role in calculation of band structure and then band discontinuities at the interface of proposed multilayer structure. Our primary concern is to investigate direct interband transition which involves obtaining bandstructure at band edge (Γ-valley conduction band) in GeSn QW by evaluating strain dependent band profile. Moreover, we have also assumed no coupling between the conduction band and valence bands, which is an appropriate estimation for group IV alloys. In this context, model solid theory suggested by Van de Walle, is well suited to our proposed model [34]. Model solid theory is said to be one of the most reliable method to calculate band line ups and their alignment at zone center (Γ-valley) in a strained heterostructure. So we followed this theory to calculate band profile in ΓCB conduction band, HH band and LH band for both well and barrier.

3.3. Coupled Schrodinger Poisson Selfconsistent Solution

After obtaining band profile, Eigen state energy of each band is required in order to evaluate direct absorption characteristics of QW. We obtained quantized energy states for Γ-CB, LH and HH band in QW by solving coupled Schrödinger and Poisson equation self consistently. Self–consistent solution is required to study the quantum confinement effect of carriers in QW more accurately considering variation in charge density of carriers. The Schrödinger equation with effective mass approximation and considering the strain effect is considered in our analysis and is given as [35]:

$$\left[\frac{-\hbar^2}{2}\frac{\partial}{\partial z}\frac{1}{m_j}\frac{\partial}{\partial z}+\frac{\hbar^2 K_t^{\,2}}{2m_j}+V_j(z)\right]\psi = E_j\psi\,, \;(\qquad (1)$$

where ħ is the Planck's constant, z is the position variable, K_t is the transverse wave vector, ψ is the wave function, E is the Eigen energy, m and V are the effective mass and band profile respectively. Suffix X stands for type of band e.g., j=c for Γ conduction band, j=hh for HH valence band and j=lh for LH band. As the Γ valley is of only interest here, the transverse wave vector, Kt is taken as zero. The equation is solved using Finite Difference Method (FDM) to obtain Eigen energies and wave function in the well [36]. The whole region of interest is divided into N number of small elements of equal width, and the equation is solved for each of the elements.

After obtaining Eigen energies and their corresponding wavefunctions, the position dependent charge density of carriers in well is calculated by summing the square of the wave function at each spatial element (Δz) and multiplying this quantity by the number of carriers in each bound state. The expression for electron density (n(z)) and hole density (p(z)) in well is given as [37]:

$$n(z) = \sum_{n} N_n \left|\psi_n^{CB\Gamma}(z)\right|^2 ; \qquad p(z) = \sum_{m} N_m \left|\psi_m^{HH/LH}(z)\right|^2 , \tag{2}$$

where n and m are the number of subbands in ΓCB, valence band (LH and HH) respectively, N_n is the number of electrons in n^{th} sub-band in conduction band and N_m is number of holes in mth subband of HH band and LH band.

The obtained position dependent carrier charge densities (n(z) and p(z)) are then used in Poisson equation. Poisson equation relates the potential to the charge density distribution as given in eqn.3 [37].

$$\frac{d^2V}{dz^2} = -\frac{q}{\varepsilon}\left(n(z) - p(z) + N_A - N_D\right) \tag{3}$$

where n(z) and p(z) are the electrons and holes charge density distribution as obtained above. N_A and N_D are the acceptor and doping impurities in QW respectively and V is the spatial electrostatic potential in QW. Dirichlet and Neumann boundary conditions are also considered while solving the Poisson equation. Poisson equation was also solved by using finite difference numerical technique. In order to obtain self-consistent Eigen state energies both Poisson equation and Schrödinger equations are solved simultaneously until their solutions are converged [38].

3.4. Evaluation of Absorption Coefficient

After calculating Eigen energies and wavefunctions for Γ-CB, HH band LH band, direct interband transition characteristic of the QW structure is studied. Absorption coefficient is evaluated for QW with the help of Fermi golden rule and using the following mathematical expression, for absorption coefficient α [35]:

$$\alpha(\hbar\omega) = \frac{\pi q^2}{n_r c \varepsilon_0 m_0^2 \omega} \sum_{n,m} \left|I_m^n\right|^2 \cdot \left|P_{CV}\right|^2 \cdot \rho_{r\,2D} \cdot \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{\left(\hbar\omega - E_0 + E_{cn} - E_{vm}\right)^2}{(2\sigma)^2}\right](f_v - f_c), \tag{4}$$

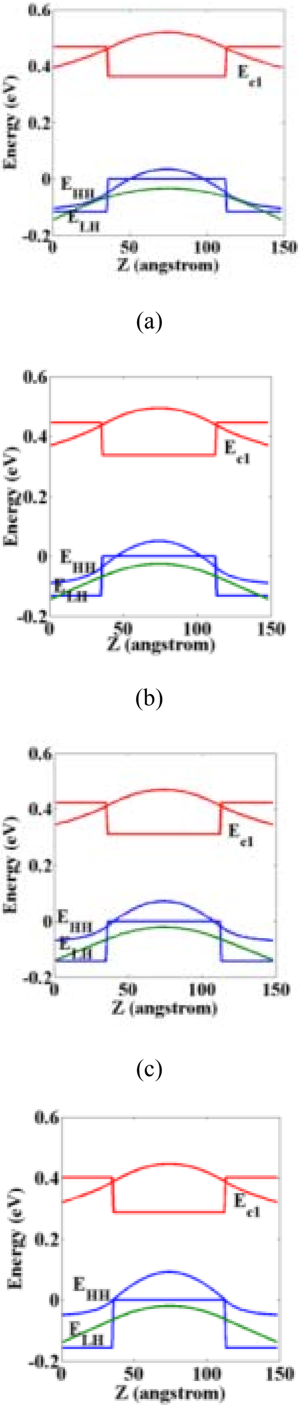
where, ω is the photon frequency, q is the electronic charge, c is the speed of light, n_r is the refractive index of well, ϵ_0 is the static dielectric constant, m_0 is the electron rest mass. E_0 is the direct band gap of $Ge_{1-x}Sn_x$ which is calculated by linear interpolation of direct band gap of Ge and Sn considering bowing parameter. E_{cn} and E_{vm} are the bound state Eigen energies for n_{th} subband in Γ conduction band, and for m_{th} subband in valence band (v=hh for HH band, v=lh for LH band) respectively. I is the overlap integral of the Γ conduction subband wave function and valence subband wavefunction given by following equation.

ρr_{2D} is reduced joint density of states in QW. QW is assumed to be undoped in this work (ideal case), only valence band is filled with carriers so carrier probability occupancy of conduction band is taken as zero (f_c=0, f_v=1). Gaussian line shape function is also considered for inhomogeneity in GeSn alloy. P_{cv} is momentum matrix element between conduction band and valence band for Bloch state. It is a key parameter to evaluate absorption in both bulk and nanostructures. Indeed, its magnitude value indicates the strength of the interaction between photon with electron. Moreover under compressive strain TE mode is dominant than TM mode. Hence, TE polarization which parallel to the plane of QW layer is assumed in present study. In TE mode momentum matrix element of HH-Γ-CB transition is much greater than that of LH- ΓCB Γ transition at Kt=0.

4. Results and Discussions

In this study, Sn concentration in Ge1-xSnx quantum well layer is varied from 0.15 to 0.18 to obtain quantum mechanical characteristic of strain balanced quantum well and then direct absorption characteristic. As for compressive strained GeSn direct band gap nature induced in GeSn layer for x≥ 0.15 [39]. Thus the required concentration of Sn should be at least 15% in $Ge_{1-x}Sn_x$ layer. Moreover, beyond 0.18, the inter layer strain increases and it is intolerable and infeasible in actual situations.

The calculated band profile (band offset of Γ conduction band and heavy hole band) with Eigen state energies (E_{c1} for ΓCB, E_{HH} for HH band and E_{LH} for LH band) for QW at different Sn concentration is shown in Fig. 2. It is clearly observe that HH band (E_{HH}) is up shifted in comparison to light hole band profile. This is attributed due to compressive strain in the well. The band offsets of Γ conduction band and heavy hole band are sufficient large to cause quantum confinement effect of carriers. With increasing in Sn concentration, the shifting of E_{HH} in upward direction increases and bad gap also decreases subsequently. It can be also observed that Eigen wave function of LH band is weakly confined in the well. This is due to a very small negligible band offset for LH band. It also ensure that only HH-ΓCB (E_{HH}-E_{c1}) transition will be dominated in this case. Absorption coefficient spectra (α) for different x are plotted as a function of wavelength and is shown in Fig. 3. Due to higher optical matrix element of HH to ΓCB transition for TE mode, LH-ΓCB transition is ignored in this study.



(a)

(b)

(c)

(d)

Fig. 2. Plot of band profile, Eigen energies and wave functions for different values of x. (a) x=0.15, (b) x=0.16, (c) x=0.17, (d) x=0.18.

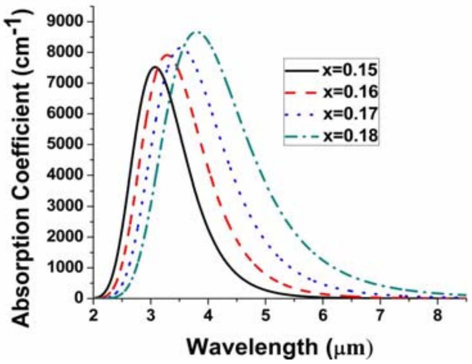


Fig. 3. Plot of absorption coefficient (α) for HH- ΓCB direct transition. versus wavelength for different values of x.

The figure clearly reveals that significant absorption for HH to ΓCB transition is observed in infrared range of wavelength (3-5μm). With increasing in Sn concentration peak absorption wavelength shifted to higher wavelength region. This red shifting is due to the lowering of the energy band gap of GeSn with increasing Sn concentration. It is also observed that with increasing Sn concentration, absorption increases.

4. Conclusions

This works throws light on the potential of Tin Incorporated Group IV alloy. It gives more emphasis on GeSn allys. Initially the motivation behind incorporation of Tin is briefly explained by explaining the basic reason and need behind this concept.

Then a detailed review and background of Tin incorporated Group IV alloy especially GeSn is elaborated along with recent advancement in its fabrication. In addition the origin of Tin and the initial work of Tin incorporation are also highlighted in this section. Also, In this section the various challenges regarding fabrication of GeSn alloy from very beginning is provided. The concept of strain can also play a very crucial role in deciding the structure of the proposed device. The importance of strain balanced structure is also briefly explained.

Later on, this paper explores the potential of GeSn quantum well layer to be used in low cost monolithic photosensitive devices for mid infrared sensing applications. Direct interband absorption is plotted for different Sn content of well for dominant HH- ΓCB transition. Sn content is selected in range of 15% to 18% to provide a direct band gap in the active layer as well as free the proposed structure from defect like dislocation, imperfection due to decrement of critical thickness at higher Sn content.

The result depicts a significant absorption in 3-5 μm range of wavelength. In addition, increment in absorption with Sn concentration is also observed. Thus this quantum well structure is viable to be used as a low cost mid-infrared sensor.

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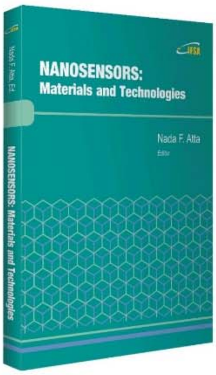
Published by International Frequency Sensor Association (IFSA) Publishing, S. L., 2017.
(http://www.sensorsportal.com).

NANOSENSORS:
Materials and Technologies

Hardcover: ISBN 978-84-616-5378-2
e-Book: ISBN 978-84-616-5422-2

Nada F. Atta, Ed.



Nanosensors: Materials and Technologies aims to provide the readers with some of the most recent development of new and advanced materials such as carbon nanotubes, graphene, sol-gel films, self-assembly layers in presence of surface active agents, nano-particles, and conducting polymers in the surface structuring for sensing applications. The emphasis of the presentations is devoted to the difference in properties and its relation to the mechanism of detection and specificity. Miniaturization on the other hand, is of unique importance for sensors applications. The chapters of this book present the usage of robust, small, sensitive and reliable sensors that take advantage of the growing interest in nano-structures. Different chemical species are taken as good example of the determination of different chemical substances industrially, medically and environmentally. A separate chapter in this book will be devoted to molecular recognition using surface templating.

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