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Growth and characterization of $Ge_{1-x}Sn_x$ alloys grown on Ge(001) and GaAs(001)

H. Pérez Ladrón de Guevara
Instituto Tecnológico de San Luis Potosí
Avenida Tecnológico S/N Km. 1 carretera a Rio Verde, C. P. 78437, San Luis Potosí, S.L.P.,Mex.

A. G. Rodríguez, H. Navarro-Contreras, M. A. Vidal
Instituto de Investigación en Comunicación Óptica (IICO), Universidad Autónoma de San Luis Potosí
Avenida Karakorum 1470, Lomas 4ta sección, C.P. 78210, San Luis Potosí, S.L.P.,Mex.

Single crystal $Ge_{1-x}Sn_x$ alloys were grown on Ge(001) and GaAs(001) substrates using a RF magnetron Sputtering. HRXRD and Raman spectroscopy were used to determine the Sn concentration of the alloys, HRXRD also shows that alloys with Sn<0.04 are pseudomorphic. Optical properties of the alloys were analysed in order to determinate the band gap transitions.

Keywords:

1. Introduction

One of the most fascinating ideas in modern semiconductor physics represents the realization of direct energy-gap material based fully on group IV elements Single crystal $Ge_{1-x}Sn_x$ alloys have interesting optical and electrical properties. These alloys have been reported to transform from indirect to direct fundamental band gap for x larger than 0.12.[1] Because of this property they open the possibility to develop totally based group IV optelectronic infrared materials systems. The $Ge_{1-x}Sn_x$ alloys exhibit the first direct band gap tunable from $0.614 > E_{DG} > 0.346$ eV for x = 0.06 to 0.15, [1,2] but it is expected that at higher Sn (~0.4) concentrations the E_{DG} decreases to 0 eV [3]. In addition, $Ge_{1-x}Sn_x$ would be expected to exhibit high carrier mobility because of a lower effective mass than that of the Ge and the lack of polar optical scattering [3,4] inherent to III-V materials. Thus this relatively new semiconductor alloy is the only known example of a direct band gap semiconductor among the compounds which can be formed from column IV elements.

In this work we report the structural, Raman, and optical characterization of $Ge_{1-x}Sn_x$ alloys obtained by RF magnetron sputtering grown on two different substrates Ge(100) and GaAs(100) with Sn concentration up to 14%.

2. Experimental Procedure and analysis.

In the HRXRD analysis we used the Expressions of Macrander[5] defined for asymmetrical diffraction planes (figure 1) where $\Delta\omega^+=\Delta\theta+\Delta\tau$ and $\Delta\omega^-=\Delta\theta-\Delta\tau$ are defined for these planes. Then we obtain the relations

$$\Delta\theta = \frac{\Delta\omega^+ + \Delta\omega^-}{2}$$

$$\Delta\tau = \frac{\Delta\omega^+ - \Delta\omega^-}{2}$$

$$a_\perp = a_s \frac{\cos\tau_s}{\cos\tau_l}\frac{\operatorname{sen}\theta_s}{\operatorname{sen}\theta_l} = a_s \frac{\cos\tau_s}{\cos(\tau_s+\Delta\tau)}\frac{\operatorname{sen}\theta_s}{\operatorname{sen}(\theta_s+\Delta\theta)}$$

$$a_{//} = a_s \frac{\operatorname{sen}\tau_s}{\operatorname{sen}\tau_l}\frac{\operatorname{sen}\theta_s}{\operatorname{sen}\theta_l} = a_s \frac{\operatorname{sen}\tau_s}{\operatorname{sen}(\tau_s+\Delta\tau)}\frac{\operatorname{sen}\theta_s}{\operatorname{sen}(\theta_s+\Delta\theta)}$$

These relations are obtained from Braggs's law and trigonometric expressions. In these expressions the elastic constants of the film are not necessary. The values of $\Delta\omega^+$ and $\Delta\omega^-$ are obtained from HRXRD measurements. They are defined as the separation between the maximums of the diffraction peeks in the Rocking Curves (figure 2) in the asimetric planes (in this case $\Delta\omega^+$ and $\Delta\omega^-$ are the separation in the planes (-1-15) and (115) respectively).

The lattice parameters of the alloys, the Sn concentration and the relaxation of the films were found using the Macrander´s relations and assuming the Vegard´s law. It's found that the alloys with low Sn concentration x<0.04 have pseudomorphic characteristics, since the in-plane lattice parameters in both $Ge_{1-x}Sn_x$ grown on Ge and GaAs have the same value of the substrate lattice parameter (figure 3).

The thickness of the $Ge_{1-x}Sn_x$ alloys that presents pseudomorphical characteristics were compared with several critical thickness models [6-9] (figure

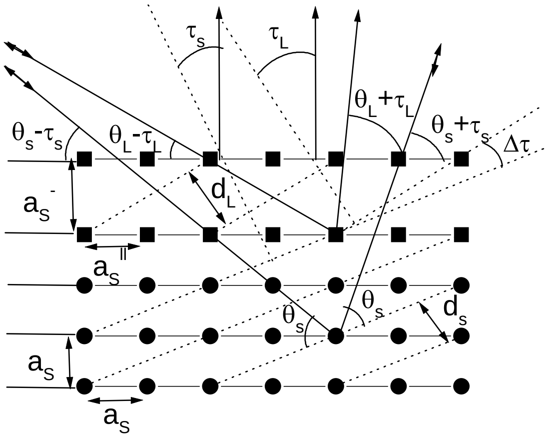

Figure 1. Diagram of a X-Ray diffraction on asymmetrical planes.a_s is the substrate lattice parameter, $a_L^{\perp}$ and $a_L^{\parallel}$ are the in-growth and in-plane latitice parameters of the layer respectivaly, θ_s, θ_L, τ_s and τ_L are the bragg´s angles and the tilt angle of the plane of the substrate and layer respectivaly.

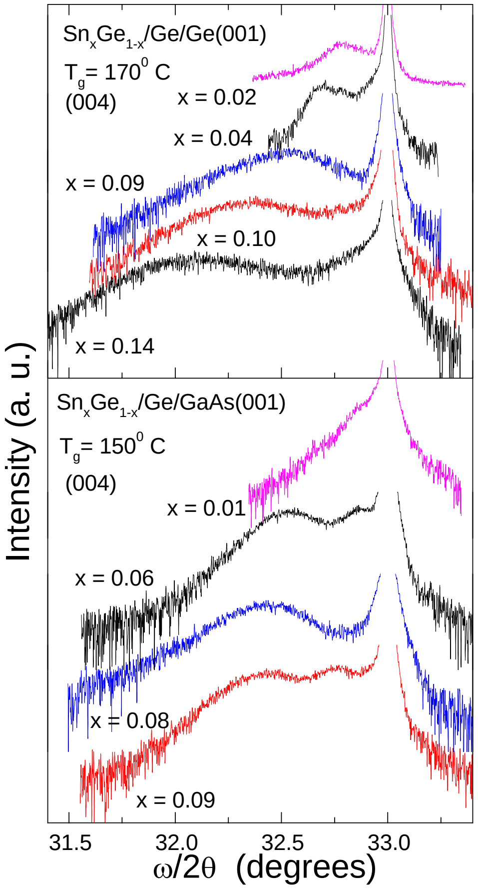

Figure 2. HRXRD rocking curves on the (004) plane of $Ge_{1-x}Sn_x$ alloys grown on Ge(100) and GaAs(100) substrates. The curves show the precense of epitaxial $Ge_{1-x}Sn_x$ layers. The Sn concentration is also shown for each curve.

4). It was found that the only model in agreement with our results is the People and Bean model [9], this model was proposed for the $Ge_{1-x}Si_x$ alloy. This is a group IV alloy like $Ge_{1-x}Sn_x$ alloy and we believe that this is the reason for the agreement in the results.

Raman spectroscopy was used to confirm the existence of the $Ge_{1-x}Sn_x$ alloys and as another way to determinate the Sn concentration according to the linear relation $\Delta\omega_{GeSn} = \omega_0 - 76.8\text{cm}^{-1}$ [10] ¨ for the Raman shift of the peak of Germanium from $\omega_0 = 301.0$ cm^{-1} (figure 5). It was found that the Sn concentration predicted by the Raman shift of the alloys is very near to the Sn concentration determinate by HRXRD as shown in figure 6. This results probes that Raman spectroscopy is another way to determine the Sn concentration of the alloys. The optical properties of the alloys were analysed using a FT-IR interferometer for measuring the transmittance of the $Ge_{1-x}Sn_x$ alloys. Transmittance measurements were performed for this alloys (figure 7) and hence the absorption coefficient were obtained for each sample (figure 8). The energy bandgap transition values were obtained by fitting the absorption edge with a model that includes the direct, indirect transitions and the Urbach's tail energy. Also the critical points of the transmittance and the absorption coefficient, the parabolic approximations and the differentiates of this curves were considered.

The determination of the change between indirect to direct band gap is not easy for Sn concentrations $0.6 < x < 0.13$ due to the proximities of the gaps sometimes only a transition value is observed. However it's possible to separate the gap values in alloys with higher Sn concentration. The experimental results obtained are not in agreement with the Tight-Binding model [3] or the Pseudo-Potential model [11] previously proposed. The data obtained are very nearly to the Potential of Deformation theory [12] results published recently and corroborated by FT-IR [1,2] and spectroscopic ellipsometry [13], these results are shown in figure 9.

Although the change from indirect to direct band gap is expected by Potential of Deformation Theory around Sn = 10%, we only observe experimentally this change to Sn = 14%.

Conclusions

In conclusion, we have shown that it is possible to grow crystalline layers of $Ge_{1-x}Sn_x$ on Ge and GaAs substrates, with Sn concentration up to x = 0.14. Coherent $Ge_{1-x}Sn_x$ layers ($x < 0.04$) can be grown on Ge substrates according to People and Bean critical thickness model and therefore have

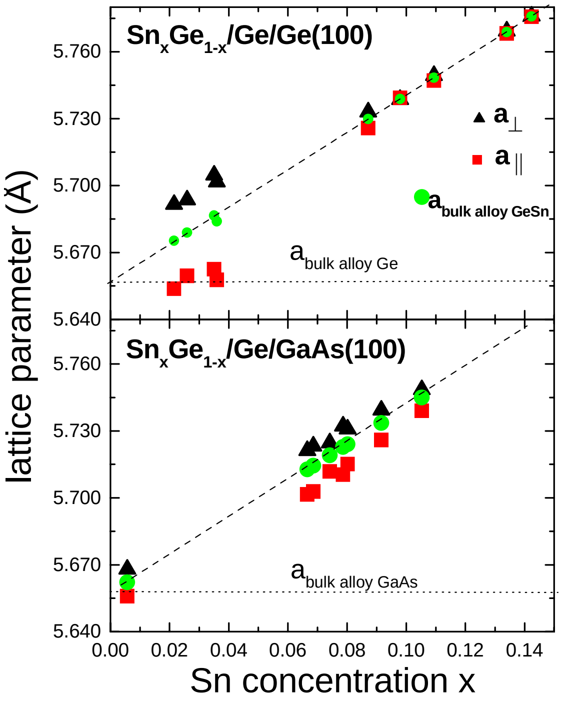

Figure 3. The $a_\perp$ (in-growth), $a_{||}$ (in-plane) and a_0 (bulk) lattice parameters of the $Ge_{1-x}Sn_x$ alloys are shown as function of Sn concentration.

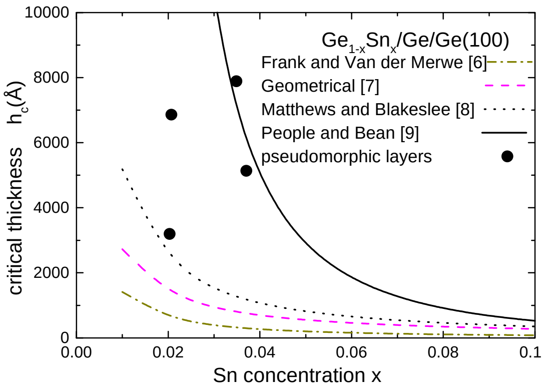

Figure 4. The thickness of the pseudomorphical $Ge_{1-x}Sn_x$ layers is compare with several critical thickness models reported everywere. [6-9]

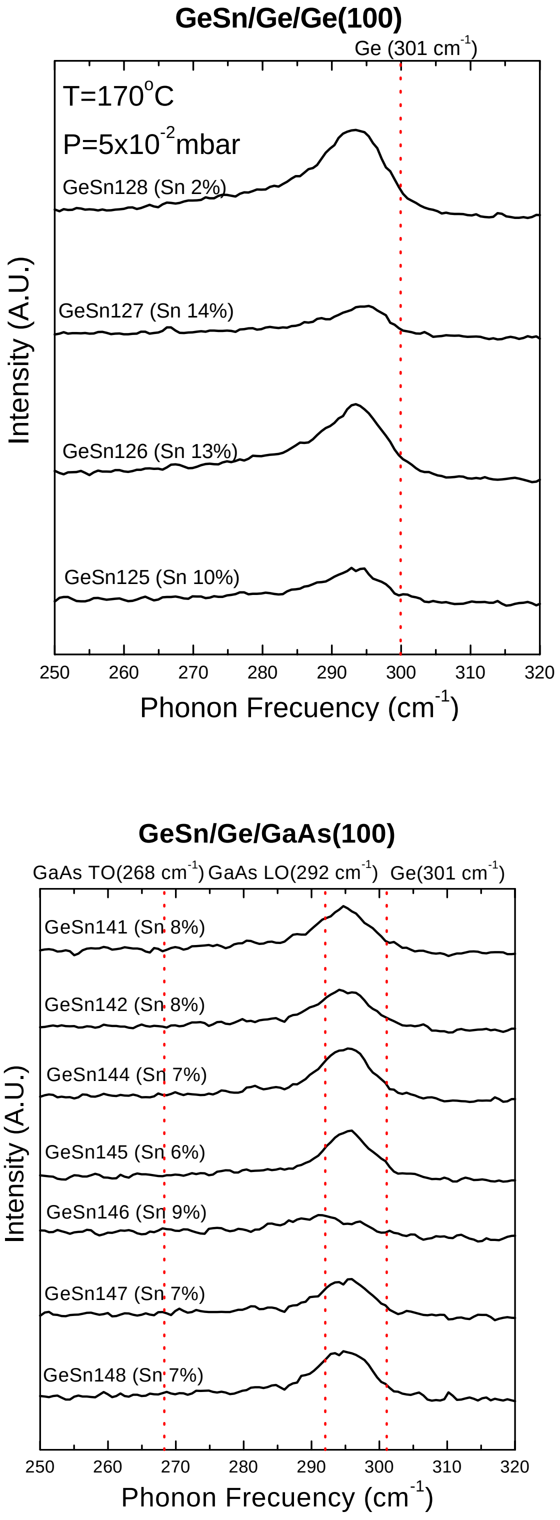

Figure 5. Raman measurements of the $Ge_{1-x}Sn_x$ alloys grown on Ge(100) and GaAs(100) substrates. The doted lines indicate the positions of the LO and TO modes of Ge and GaAs. The Sn concentration of the alloys is also shown.

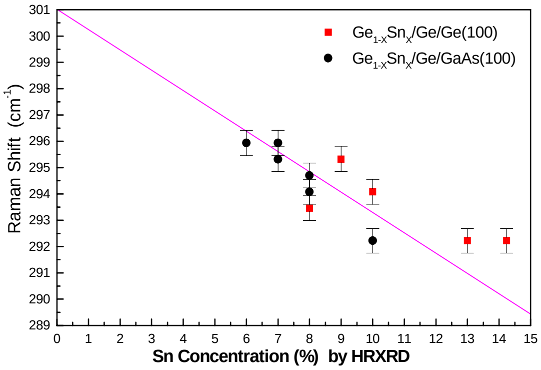

Figure 6. Raman shift of the $Ge_{1-x}Sn_x$ alloys compare with the Sn concentration determined by HRXRD. The solid line is the Raman shift $\Delta\omega_{GeSn} = \omega_0 - 76.8cm^{-1}$ [10] reported for $Ge_{1-x}Sn_x$ alloys.

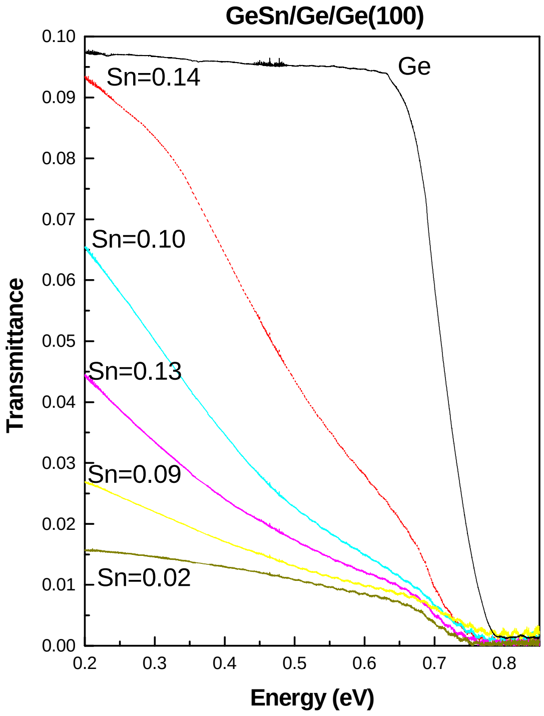

Figure 7. Transmittance measurements of the $Ge_{1-x}Sn_x$ alloys grown on Ge(100) substrates. The Sn concentration of th e alloys is shown for each curve.

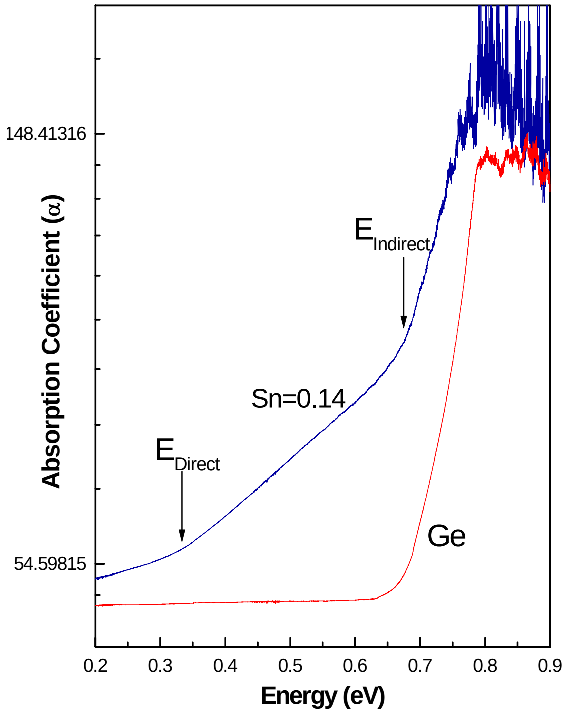

Figure 8. Absorption coefficient obtained from the transmittance measurements of the $Ge_{0.86}Sn_{0.14}$ alloy. The determined direct and indirect band gap transitions of the alloy are shown.

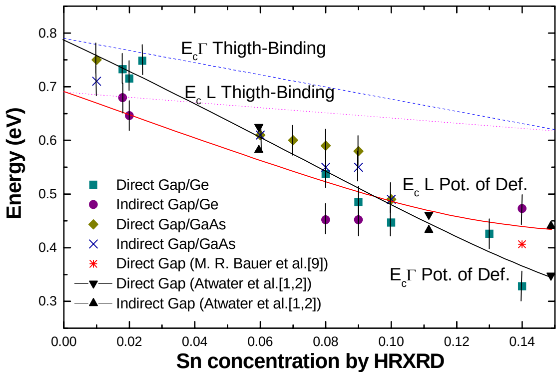

Figure 9. Experimentally energy Band Gap values of the $Ge_{1-x}Sn_x$ alloys compared with the predicted by the Potential of Deformation Theory. The Sn concentration values in the graph were determined by HRXRD.

epilayers that are totally dislocations free. The $Ge_{1-x}Sn_x$ alloys presents a tunable band gap. The values of the Direct and Indirect band gaps are very similar to the values predicted by the Potential of Deformation Theory. A direct transition is experimentally observed for alloys with Sn concentration up to 0.14.

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