

Determination of the optical energy gap of $\text{Ge}_{1-x}\text{Sn}_x$ alloys at 4K

H. Pérez Ladrón de Guevara

Universidad de Guadalajara-Centro Universitario de los Lagos
Enrique Díaz de León s/n col. Paseo de la Montaña, Lagos de Moreno, Jal. 47460

A. G. Rodríguez, H. Navarro-Contreras, and M. A. Vidal

Instituto de Investigación en Comunicación Óptica (IICO), Universidad Autónoma de San Luis Potosí
Álvaro Obregón 64, San Luis Potosí, S.L.P. 78000

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The optical energy gap of $\text{Ge}_{1-x}\text{Sn}_x$ alloys ($x \leq 0.14$) has been determined from transmittance measurements at 4K using a Fast-Fourier-Transform Infrared Interferometer (FFT-IR) attached to a helium refrigerator. Our results show that the energy gap changes due to the Sn concentration of the alloys. We also show that low temperature increases the energy gap transitions for alloys with low Sn concentrations. By increasing gradually the Sn concentration in alloys the energy gaps decreases, but for $x > 0.13$ alloys, direct energy gap transitions are lower than energy gap obtained at room temperature. These results are according to the theory predicted results at low temperatures.

Keywords: Sputtering; FFT-IR; HRXRD

1. Introduction

$\text{Ge}_{1-x}\text{Sn}_x$ alloys are very interesting due to the possibility of obtain a direct and modulated energy gap semiconductor based totally on group IV elements for infrared optoelectronics applications [1-3], the direct energy gap just depends on the Sn concentration of the alloy. The achievement of the alloy is possible by using growth techniques like Pulsed UV Laser Crystallization [4], MBE [5-7], CVD [8], UHV-CVD [9-13], and Sputtering [14, 15]. The growth conditions provide a good crystal quality in order to obtain $\text{Ge}_{1-x}\text{Sn}_x$ alloys with enough Sn concentration for reaching the crossover between indirect (semi metal) to direct energy gap semiconductor.

Although the presence of direct energy gap transitions (~ 0.5 to 0 eV) has been previously shown for $\text{Ge}_{1-x}\text{Sn}_x$ alloys with Sn concentrations lower than originally expected $0.09 < x < 0.28$ [3, 19-21], the determination of the behaviour of the direct energy gap transition at low temperatures has not been complete reported. At the moment, it has been reported the energy gap behaviour for $\text{Ge}_{1-x}\text{Sn}_x$ alloys with low Sn concentrations ($x < 0.05$) at 15 K [19]. In this work we present the results obtained from transmittance measurements for alloys with Sn concentrations until $x = 0.14$ at 4 K.

According to reference [19] direct energy gap transitions in $\text{Ge}_{1-x}\text{Sn}_x$ alloys is predicted to decrease like

in the group IV $\text{Ge}_{1-x}\text{Si}_x$ alloy due to nonlinear (bowing) parameters. By applying the Coherent Potential Approximation (CPA) instead of the Virtual Crystal Approximation the nonlinearity results are justified. One result of these work is that direct energy gap transitions decreases abruptly from 0.89 eV in pure Ge until ~ 0.4 eV for $\text{Ge}_{0.86}\text{Sn}_{0.14}$ alloys at 15 K, where practically direct energy gap transitions has the same energy than those obtained at room temperature. According to CPA alloys with $x > 0.13$ are predicted to have a direct energy gap transition in LT less than obtained in RT. Lower direct energy gap transitions must be obtained at lower temperatures ($T < 15$ K). This fact is expected from the relationships between bowing parameters versus Sn concentration and low temperature.

2. Experimental Procedure

$\text{Ge}_{1-x}\text{Sn}_x$ alloys were grown in a R. F. Magnetron Sputtering system on Ge (100) substrates with a base pressure better than 1×10^{-7} mbar and Ar of high purity (99.999%). The targets, Ge(99.999%) and Sn(99.999%) were of 10 cm in diameter with a 5 cm separation between target and samples. The power of the Ge(99.999%) and Sn(99.999%) targets varied between 50-60 watts in order to obtain alloys with different Sn concentration.

Previously to growth, Ge substrates were ultrasonically

Table 1. Experimental direct energy gap transitions of $\text{Ge}_{1-x}\text{Sn}_x$ alloys obtained at Room and Low Temperatures, the maximum error bar in the determination of the direct energy gap transitions is also included.

Sn (X)	E_g at RT (eV)	E_g at LT (eV)
0.017	0.74 ± 0.02 eV	0.85 ± 0.02 eV
0.06	0.63 ± 0.02 eV	0.68 ± 0.02 eV
0.07	0.57 ± 0.02 eV	0.58 ± 0.02 eV
0.08	0.53 ± 0.02 eV	0.54 ± 0.02 eV
0.09	0.50 ± 0.02 eV	0.53 ± 0.02 eV
0.1	0.45 ± 0.02 eV	0.52 ± 0.02 eV
0.14	0.33 ± 0.02 eV	0.39 ± 0.02 eV

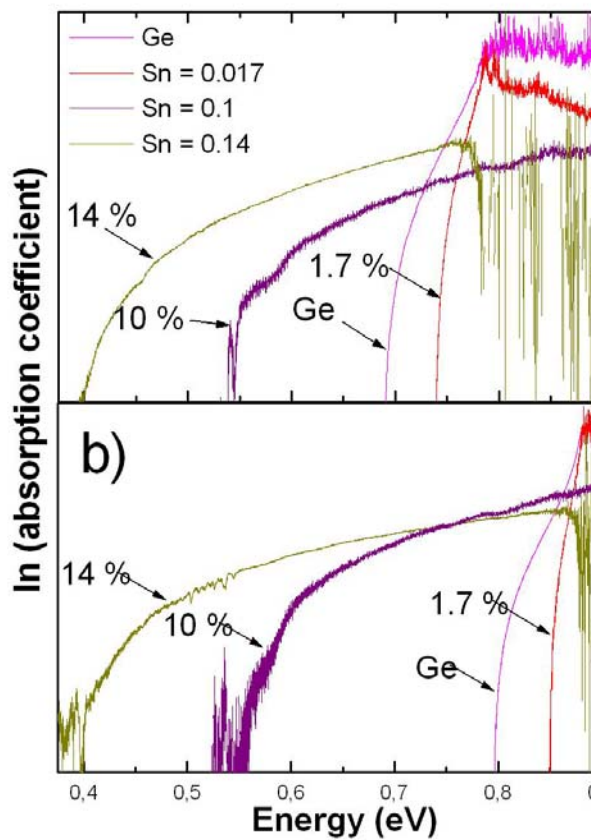


Figure 1. Absorption coefficients of $\text{Ge}_{1-x}\text{Sn}_x$ alloys with Sn = 0.017, 0.06, 0.1 and 0.14 at a) Room Temperature and b) Low Temperature respectively.

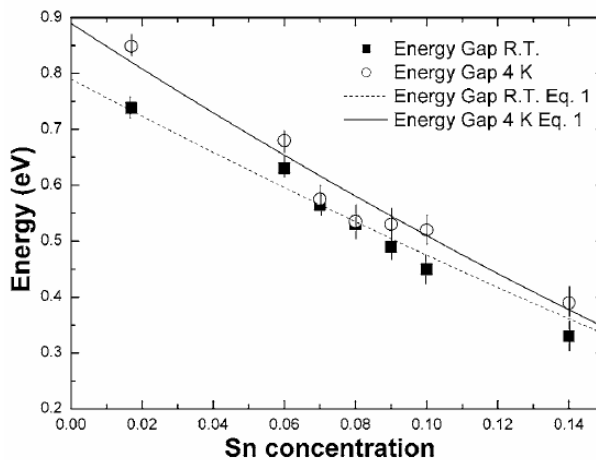


Figure 2. Experimental direct energy gap transitions of $\text{Ge}_{1-x}\text{Sn}_x$ alloys obtained at Room and Low Temperatures, nonlinear behaviour predicted at RT and 15 K [22] is also shown.

decreased in successive rinses of trichloroethylene, acetone, and methanol for 10 minutes. After degreasing, the samples were ultrasonically rinsed in deionised water for 15 minutes and then blown dry in N_2 . Next the substrates were exposed in air to a 33 mW/cm^2 of radiation from a UV lamp (line emission in 366 nm) during 30 minutes. This procedure is done in order to remove the native oxide layer and form a thin non-permeable and passive amorphous GeO_2 layer by an ultraviolet-ozone process [20]. The GeO_2 layer is easily removed by thermal desorption at temperatures $T_d \geq 390 \text{ }^\circ\text{C}$ for times $t_d \geq 30$ minutes.

In order to have a high accuracy control in the growth temperature of the alloy, the samples were attached to the substrate holder with small steel arms creating a good thermal contact. It must be remarkable that this procedure is done because low temperature plays an important role in the $\text{Ge}_{1-x}\text{Sn}_x$ alloy growth.

A Ge buffer layer of $\sim 1700 \text{ \AA}$ thickness in all samples was grown from the desorption temperature to the growth temperature of the alloy (150 to 170 $^\circ\text{C}$). $\text{Ge}_{1-x}\text{Sn}_x$ alloy is grown by varying the exposure time of the substrates under the Ge and Sn targets for total growth times from 3 to 30 minutes. The alloys thicknesses are a few thousand Angstroms according to HRXRD and HRTEM measurements. The maximum Sn concentration obtained in the alloys is $x = 0.14$. This concentration was determined by HRXRD and Raman measurements [15].

Transmittance measurements of the samples were done in a FFT-IR spectrometer between 500 and 7500 cm^{-1} . Low temperature was reached using a cold finger attached to a helium refrigerator introduced in the vacuum chamber of the spectrometer. The maximum low temperature reached in the experiment was 4K. The windows used in the cold finger are Mylar with an optical absorption between 0.345 and 0.375 eV (In this energy region, direct energy transitions due to $\text{Ge}_{1-x}\text{Sn}_x$ alloys in the Sn concentrations range of the samples prepared are not expected, so lost information occasioned by Mylar windows is not important for this analysis). Film transmittance of the alloys was obtained by dividing the measured sample signal by substrate and Ge buffer layer transmittance signals.

3. Results

Figures 1.a and 1.b show the absorption coefficients of some $\text{Ge}_{1-x}\text{Sn}_x$ alloys with different Sn concentration obtained at RT and 4K respectively. Direct and indirect transitions are observed for a Ge(100) substrate, the expected increase in the energy gaps due to low temperature (4K) is about 0.1 eV. This shift is clearly shown in figure 1.b.

In figures 1.a and 1.b a $\text{Ge}_{0.983}\text{Sn}_{0.017}$ alloy is shown, a critical point due to the direct energy transition is very close to Ge direct energy transition, no indirect transition is clearly shown at RT and LT. In general alloys with $x < 0.06$ presents a transition attributed to the direct energy gap. This consideration is done due to the curvature of the absorption coefficient present at RT and LT and to the energy value obtained for this Sn concentration (an indirect energy gap transition must be

present at lower energies than Ge indirect energy transition).

For $0.06 < \text{Sn} < 0.1$ alloys the absorption coefficient show critical points attributed to optical transitions in RT and LT. It is difficult to determine which point is due to direct or indirect energy gap transitions directly from the absorption coefficient curvatures. We attribute this fact to the proximity of the energy gaps as is expected for these alloys in this Sn concentration range, bowing behaviour of the energy gap transitions is also attributable to this fact. Increasing the energy transitions due to LT is not as notorious as in lower Sn concentration alloys (~ 0.1 eV); however a better determination of the critical points is obtained. A $x = 0.1$ sample is shown in figures 1.a and 1.b, presence of two critical points is observed at RT and LT.

For $\text{Sn} > 0.1$ the crossover between indirect to direct energy gap transition system is already reached. Absorption coefficients show the presence of one critical point attributed to a direct energy gap transition and very close to previously reported values at RT [3, 16-18]. Again LT measurements provide a better determination of the critical points. Absorption coefficients present no measurable increases in the energy gap due to LT; this behaviour is expected from reference [19] according to Coherent Potential Approximation (CPA) at 15K.

Table 1 shows the values of the direct energy gaps transitions obtained in this work for different $\text{Ge}_{1-x}\text{Sn}_x$ alloys, the maximum error bar in the determination of the direct energy gap transitions is $\Delta E_G = \pm 0.01$ eV. This maximum error is reached in the concentration range $0.06 < x < 0.1$, near to the experimental crossover of the energy gaps.

4. Conclusions

Figure 2 plots the data shown in Table 1, plus continue and dashed lines show the direct energy gap transitions expected at RT and 15 K respectively according to the CPA presented on reference [19]. It is clear from Figure 2 that direct energy gap transitions obtained on $\text{Ge}_{1-x}\text{Sn}_x$ alloys at 4K present a non linear behaviour like in the $\text{Ge}_{1-x}\text{Si}_x$ system at RT, but at LT non linearity is bigger than obtained at RT according to theoretical predicted results. In fact nonlinearity observed at 4K is bigger than nonlinearity determined at 15 K. A crossover between direct energy transition at RT and LT it is expected. Then direct energy gap transitions at lower energies could be

obtained for alloys with higher Sn concentrations ($x > 0.14$).

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