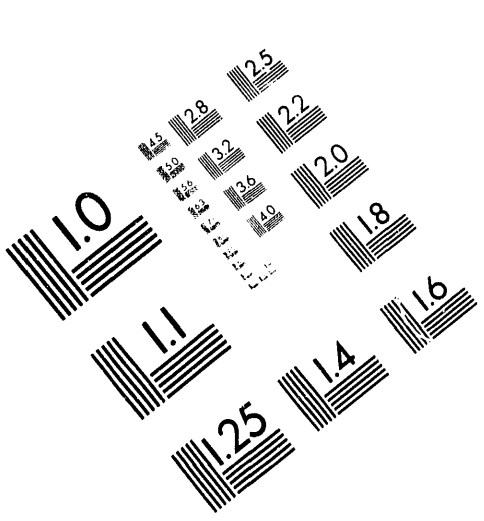

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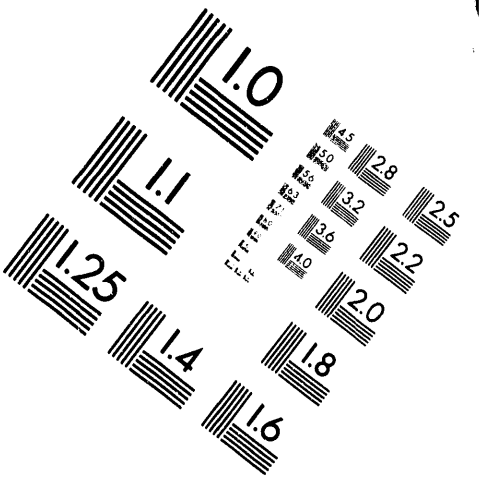

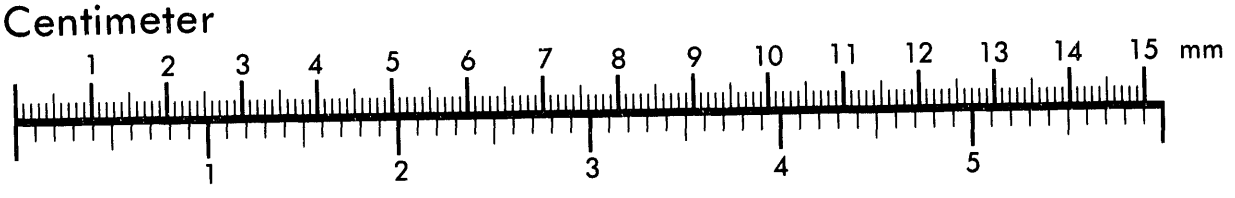

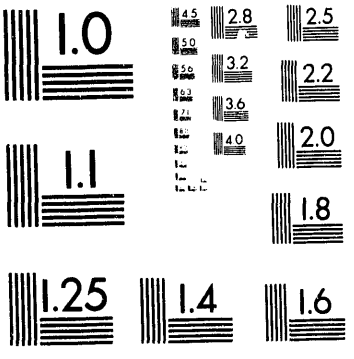

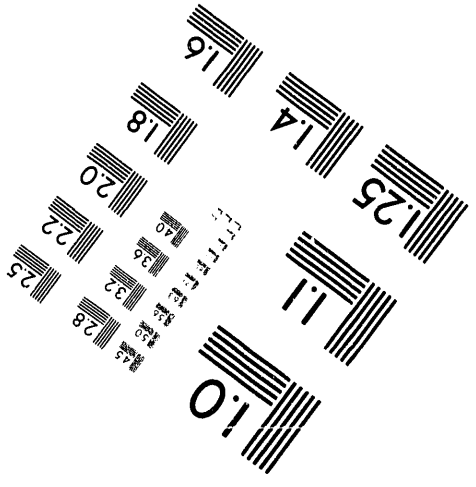

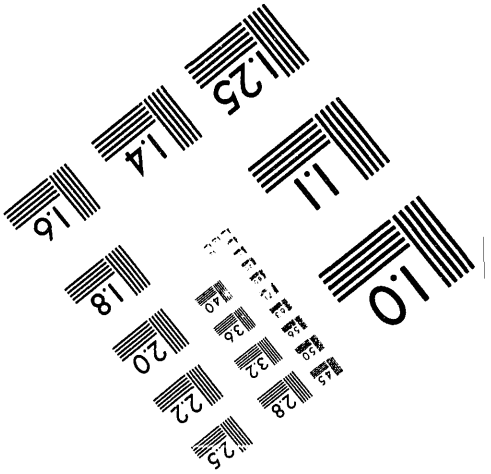

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The Growth Of $InAs_{1-x}Sb_x$/InAs Strained-Layer Superlattices By Metal-Organic Chemical Vapor Deposition

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ABSTRACT

$InAs_{1-x}Sb_x$/InAs strained-layer superlattice (SLS) semiconductors and thick epitaxial layers of $InAs_{1-x}Sb_x$ were grown under a variety of conditions by metal-organic chemical vapor deposition on InAs substrates. The III/V ratio was varied from 0.026 to 1.0 over a temperature range of 475-525 ^oC, at pressures of 200 to 660 torr and growth rates of 0.75 to 3.0 μm/hour. The composition of the ternary can be predicted from the input gas molar flow rates using a thermodynamic model. At lower temperatures, the thermodynamic model must be modified to take account of the incomplete decomposition of arsine and trimethylantimony. These layers were characterized by optical microscopy, SIMS, and x-ray diffraction. The optical properties of these SLS's were determined by infrared photoluminescence and absorption measurements. The PL peak energies of the alloys' and the SLS's are consistently lower than the previously reported values for the bandgap of $InAs_{1-x}Sb_x$ alloys.

INTRODUCTION

The growth of $InAs_{1-x}Sb_x$/InAs SLS's is being explored by us for their possible use in mid-wave, 2-5 μm infrared optoelectronic and heterojunction devices. This system was chosen because the compositions span the 2-5 μm wavelength range and they can be grown lattice matched to GaSb. Recent results by Menna et al. on a metal-organic chemical vapor deposition (MOCVD) grown 3.06 μm diode laser with a maximum operating temperature of 35 K and threshold current densities of 200 - 330 A/cm^2 indicate the potential and the need for devices operating in this wavelength range [1]. Our previous studies in the Sb rich end of this ternary system have demonstrated accurate composition control through the use of a thermodynamic model [2] and high quality infrared detectors have been made in this laboratory from doped strained-layer superlattices (SLS's) grown by MOCVD in the Sb rich end of this ternary [3].

The initial growth studies reported on here focused on the growth of $InAs_{1-x}Sb_x$/InAs heterostructures and thick epitaxial layers on InAs. The thermodynamic model used to describe composition control in the Sb rich compositions can also be used to predict the composition of As rich materials. The details of the growth conditions for $InAs_{1-x}Sb_x$/InAs SLS's and $InAs_{1-x}Sb_x$ alloys, a description of the thermodynamic model, and infrared photoluminescence and absorption measurement results are presented The applicability to infrared devices of As rich $InAs_{1-x}Sb_x$ materials is also discussed.

EXPERIMENTAL

This investigation was carried out in a previously described horizontal MOCVD system [4]. The sources of In, Sb and As were trimethylindium (TMIn), trimethylantimony (TMSb) and 100 or 0.1 percent arsine (AsH_3), respectively. Hydrogen was used as the carrier gas at a total flow of 6 SLM. The III/V ratio was varied from 0.026 to 1.0 over a temperature range of 475-525 ^oC, at total growth pressures of 200 to 660 torr and growth rates of 0.75 to 3.0 μm/h. The

growth was performed on (001) InAs substrates. InAs was cleaned by degreasing in solvents and deionized water. It was then etched for one minute in a 10:1 mixture of sulfuric acid and hydrogen peroxide, rinsed with deionized water and blown dry with nitrogen.

Sb compositions, x, reported for the $InAs_{1-x}Sb_x$ layers were determined by x-ray diffraction using a Cu x-ray source and a four crystal Si monochromator. Both the (004) and the (115) or (335) reflections were used to determine compositions [4]. Some samples were also checked for impurities using secondary ion mass spectroscopy (SIMS).

Infrared photoluminescence was measured at 14 K using a double-modulation technique which provides high sensitivity, reduces sample heating, and eliminates the blackbody background from infrared emission spectra [5]. The absorption measurements were carried out on polished samples using a Fourier transform infrared spectrometer.

RESULTS AND DISCUSSION

The growth of $InAs_{1-x}Sb_x$ and $InAs_{1-x}Sb_x$/InAs SLS's were investigated using III/V ratios between 0.026 and 1.0 over a temperature range of 475-525 ^oC, at total growth pressures of 200 to 660 torr and growth rates of 0.75 to 3.0 μm/h. The group V molar fraction of TMSb in the vapor phase [$n_{TMSb}/(n_{TMSb} + n_{AsH3})$] was varied from 0.02 to 0.55. The growth results for the As rich end of the $InAs_{1-x}Sb_x$ ternary are similar to those described previously for the Sb rich end of the ternary [5]. The growth temperature was kept below the melting temperature of InSb, 525 ^oC, due to the expected low solidus temperatures. The growth rate was found to be proportional to the TMIn flow into the reaction chamber and independent of the TMSb and AsH_3 flow.

The observed trends for the effects of input vapor concentrations on the resulting solid composition are illustrated in Figure 1. Previous results could be completely described by a thermodynamic model [5]. The model predicts that the thermodynamically more stable III/V

compound will control the composition. For the InAsSb system when III/V < 1, As is preferentially incorporated into the solid and the solid-vapor distribution coefficient of Sb (k_{Sb}) is < 1. This is because InAs is more stable, has a lower free energy of formation, than InSb at 475-525 °C. For III/V ratios close to one, k_{Sb} approaches one and for III/V ≥ 1, $k_{Sb} = 1$. When III/V ≥ 1, all of the group V materials, As and Sb, will be incorporated into the solid. These trends are also found for this data as illustrated in Figure 1.

However, some slight deviations from the predicted behavior of the thermodynamic model are observed for the present results. For some of the samples grown at 475 °C, k_{Sb} appears to be ≥ 1 . This can be explained by assuming that not all of the AsH_3 is decomposed at this temperature. This assumption is consistent with the reported incomplete decomposition of AsH_3 at temperatures below 500 °C [6]. The SLS's grown at 525 °C had TMSb vapor fractions between 0.3 and 0.5. Their solid compositions are predicted to be slightly higher by the thermodynamic model. This is illustrated in Figure 1 by the dashed and dotted lines which represent the predicted compositions for III/V ratios of 0.5 and 0.05, respectively. The compositions should fall between these two limits. This discrepancy can be explained by the formation of an As rich interface or diffusion of As into the Sb containing layer during growth of the superlattice. Since the x-ray diffraction patterns were somewhat broad due to the presence of dislocations, the influence of an interfacial layer could not be determined from the x-ray studies.

Selected results of the infrared photoluminescence (PL) experiments are illustrated in Figure 2. The solid line represents the literature values for the bandgap versus composition for $InAs_{1-x}Sb_x$ [7]. The open squares show the PL results for a series of $InAs_{1-x}Sb_x$/InAs SLS's where the Sb composition for the graph is the Sb composition of the $InAs_{1-x}Sb_x$ layer in the SLS. The layer thicknesses of these SLS's ranged from 41 to 85 Å. The open triangles show the PL results for three $InAs_{1-x}Sb_x$ alloys. The alloys were 1.0 to 1.7 μm thick. The PL peak energies of the alloys and the SLS's are consistently lower than the previously reported values for the bandgap of $InAs_{1-x}Sb_x$ alloys [7]. The compressive strain and quantum size effect present in these SLS structures would cause the transition energy to be greater than that of the unstrained

alloy [7]. SIMS results indicate that the purity of the epitaxial layers is comparable to that of the InAs substrate so that the PL should not be dominated by impurity levels. This low energy discrepancy could be explained by the presence of ordering, phase separation, or the presence of an interfacial layer in the SLS's caused by diffusion of the As or Sb or poor separation of the reactants in the vapor phase during switching. Previous work has shown the bandgap reduction effects of ordering in $InAs_{1-x}Sb_x$ alloys and SLS's [8]. Lowering of the PL energies in phase separated materials ($InP_{1-x}Sb_x$) has also been reported [9]. The diffusion of As and In into superlattice layers has been reported to cause a lower than expected photoluminescence peak energy in GaAs/InGaP superlattices [10]. At this time it is uncertain as to which of these phenomena is causing the observed reduction in bandgap for the $InAs_{1-x}Sb_x$/InAs superlattices and alloys.

The absorption and PL curves for a selected $InAs_{1-x}Sb_x$/InAs SLS are shown in Figure 3. The absorption curve is very broad with no distinct absorption edge as would be expected for a single phase, direct gap semiconductor. Although the energy of the PL peak and the absorption "edge" overlap, the width of the absorption and the difference in energy between the onset of absorption and the PL peak indicate that the sample might be phase separated. This result is similar to the result found for $InP_{1-x}Sb_x$ where phase separation was demonstrated by transmission electron diffraction. Work is underway to prepare transmission electron microscopy cross-sections to determine if either ordering or phase separation is present in these materials. The luminescence of the SLS's grown on lattice-mismatched InAs can be weak and broad. As mentioned above, this could be due to phase separation. The existence of dislocations is also evidenced by the width of the x-ray diffraction peaks and the cross hatched patterns observed on the surfaces of the alloys and the SLS's. The dislocations could also be contributing to the width of the PL peak and the absorption "edge".

In conclusion, we have established the growth conditions for $InAs_{1-x}Sb_x$/InAs SLS's and As rich alloys. The vapor-solid distribution coefficient for Sb can be described by a thermodynamic model. The PL peak energies of the SLS's and alloys grown under the

conditions of this study are lower than those previously reported. The lower energy anomaly could be due to ordering or phase separation. For these materials to be useful for device applications, they would need to be grown on a lattice matched substrate such as GaSb to eliminate the presence of dislocations. Efforts are underway to grow these SLS's lattice matched to GaSb as well as to better characterize the materials with electron diffraction.

ACKNOWLEDGMENTS

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Figure 1. Mole fraction of InSb in solid $InAs_{1-x}Sb_x$ versus group V mole fraction of trimethylantimony in the vapor. The curves are the calculated values for III/V = 1, solid line; 0.5, dashed line; and 0.05, dotted line. The open squares and circles are values for $InAs_{1-x}Sb_x$ alloys grown at 525 and 475 ^{o}C, respectively. The filled triangles and circles represent the values for $InAs_{1-x}Sb_x$/InAs SLS's grown at 525 and 475 ^{o}C, respectively.

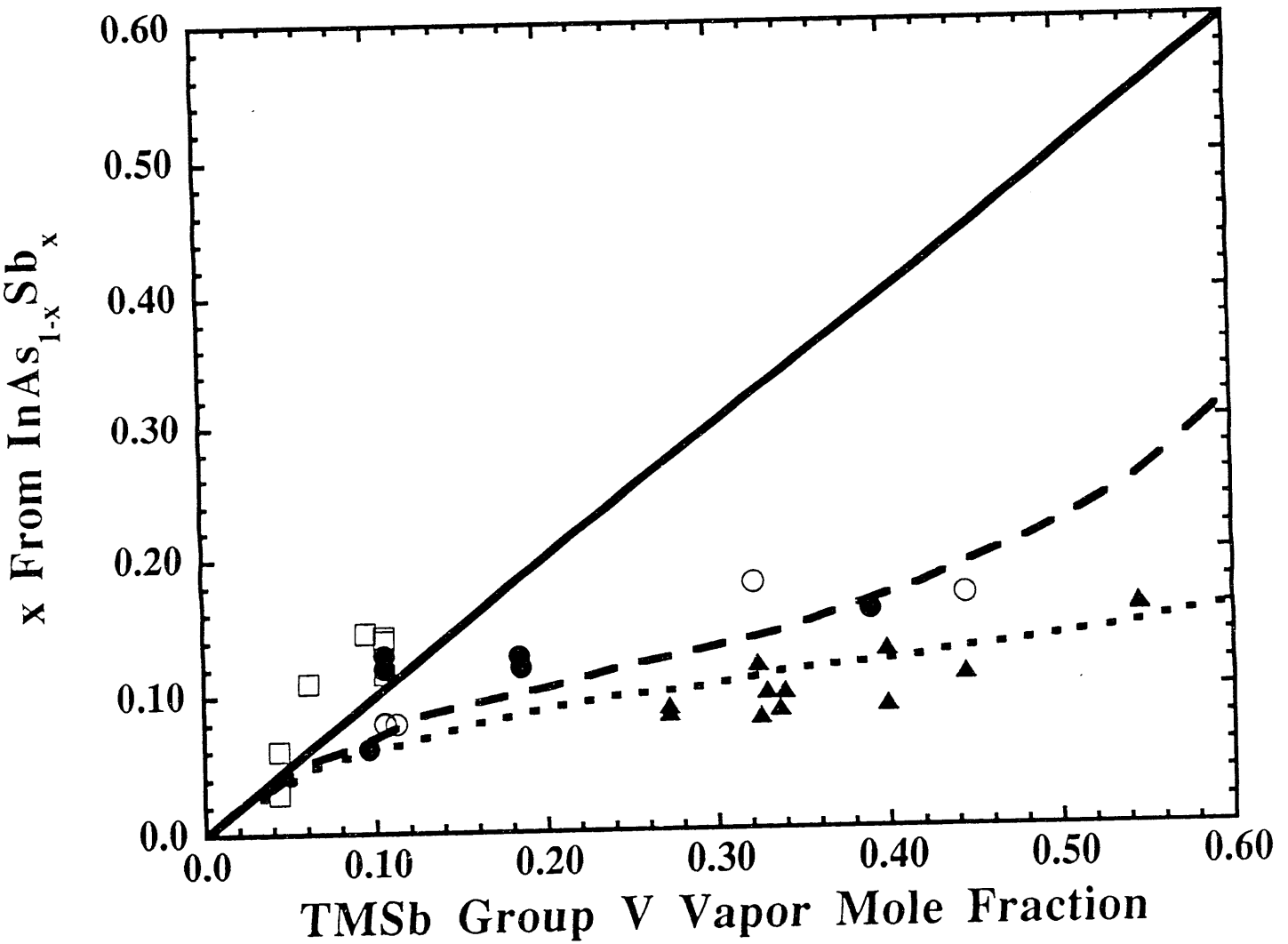

0.60
0.50
0.40
0.30
0.20
0.10
0.0
0.0
0.10
0.20
0.30
0.40
0.50
0.60
x From InAs1-xSbx
TMSb Group V Vapor Mole Fraction

Figure 2. Energy of the low temperature (10-14 K) photoluminescence peak versus composition for $InAs_{1-x}Sb_x$ alloys, triangles, and SLS's, squares. The composition was determined by x-ray diffraction and the energy represents the shortest wavelength peak in the spectrum. The bandgap versus composition curve was calculated using the equation in reference 7.

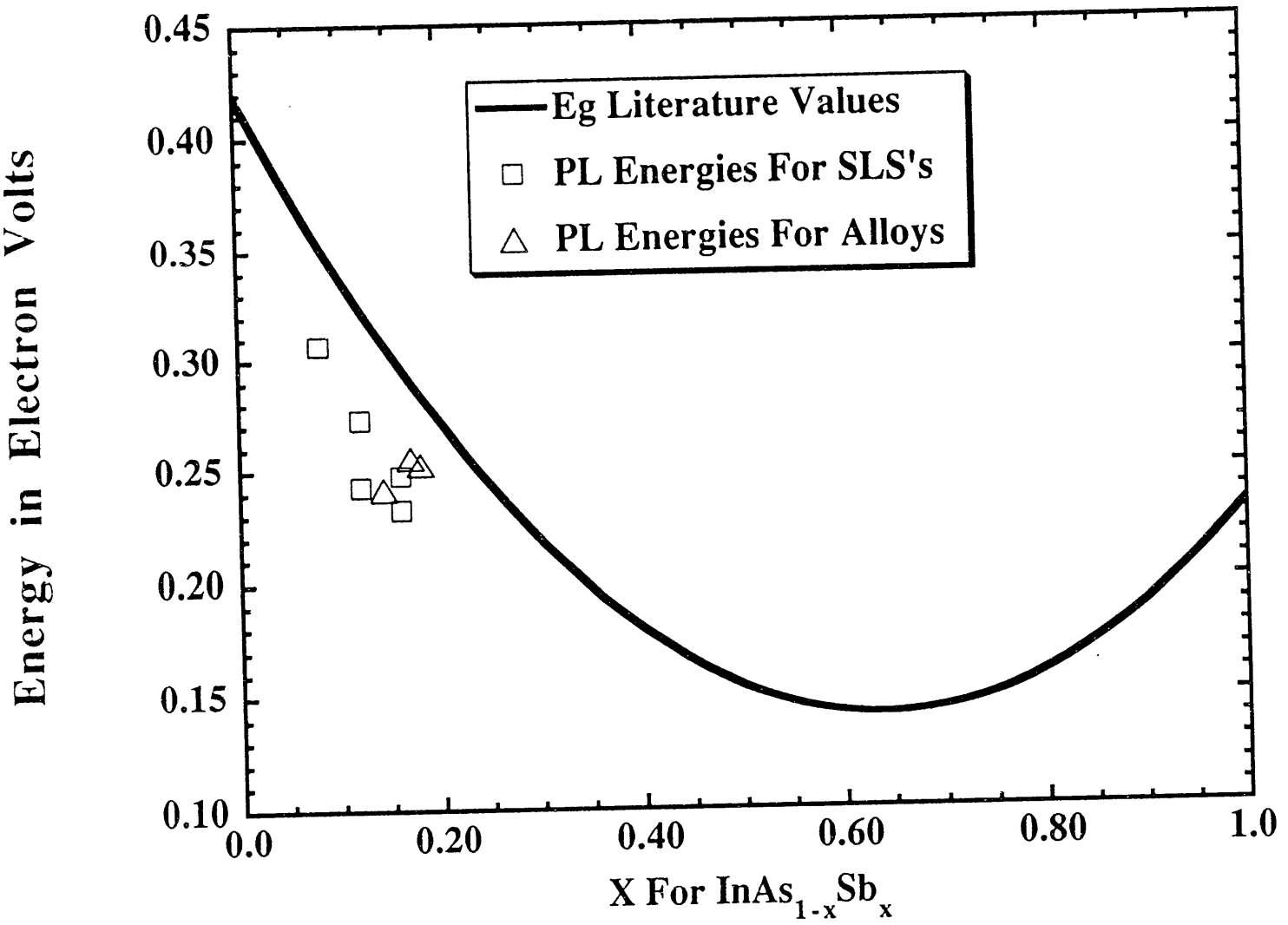
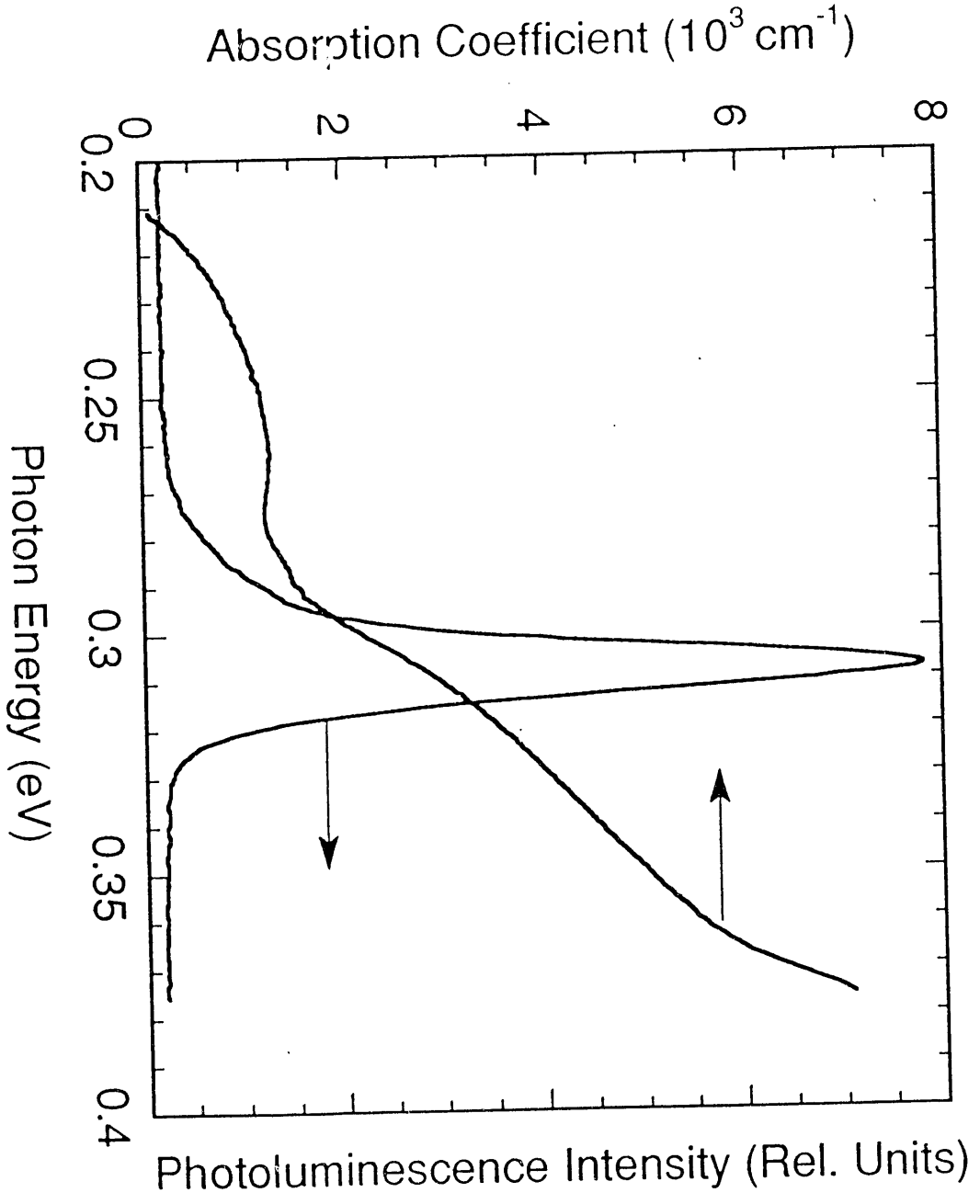

Energy in Electron Volts
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.0
0.20
0.40
0.60
0.80
1.0
X For InAs1-xSbx
Eg Literature Values
PL Energies For SLS's
PL Energies For Alloys

Figure 3. Infrared spectroscopy data showing the absorption spectra and the corresponding photoluminescence peak for an $InAs_{0.92}Sb_{0.08}$/InAs SLS grown at 525 ^{o}C a III/V ratio of 0.42 and a TMSb group V mole fraction of 0.33 (sample 1076). The sample contained alternating 79 Å layers of $InAs_{0.92}Sb_{0.08}$ and InAs. The slow increase in absorption indicates that the sample is not a typical single phase, direct bandgap semiconductor.


Absorption Coefficient (10^3 cm^{-1})
0
2
4
6
8
0.2
0.25
0.3
0.35
0.4
Photon Energy (eV)
Photoluminescence Intensity (Rel. Units)

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