RAMAN SCATTERING FROM METASTABLE (GASB)1-XGE2X ALLOYS
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(GaSb)_{1-x}Ge_{2x} ALLOYS

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RAMAN SCATTERING FROM METASTABLE 
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In an extension of earlier work (1) we have used Raman Scattering 
to reveal structural information in mixed, metastable, crystalline 
(GaSb)$_{1-x}$Ge$_{2x}$-[Ga$_{1-x}$Ge$_x$]-[Sb$_{1-x}$Ge$_x$]. These alloys were deposited on 
GaAs substrates using a multtarget r.f. sputtering system (2). 
Room temperature measurements were performed under vacuum, with 
the incoming laser beam perpendicular to a <100> plane, and photon 
polarizations along [100] directions. Figure 1 shows the Raman spectra 
of some of the mixed crystals and of the pure GaSb and Ge components (all 
normalized to same maximum peak height). When small concentrations 
of GaSb are introduced into Ge or small concentrations of Ge introduced 
into GaSb, the zone-center phonon frequency shifts, broadens, and 
becomes asymmetric. Figure 2 plots the frequencies versus "percent 
Germanium", which we define as 100x. For x<0.1 the GaSb-like phonon shows 
a TO-LO splitting, which cannot be detected for x>0.1. The frequency 
of the Ge-like optical phonon increases almost linearly with x, 
whereas the frequency of the 
GaSb-like phonon remains almost 
constant for 0.3 < x < 0.75. For 
x>0.75 this mode can no-longer be 
detected, consistent with 
expectations for behavior of 
isolated substitutional Ga and Sb 
atoms in Ge: In low concentrations 
neither atom will give a local mode 
or a gap mode. Ge, however, does 
produce a local mode as a dilute 
impurity in GaSb.

Fig. 1: Room temperature, Raman scattering of mixed 
(GaSb)$_{1-x}$Ge$_{2x}$. Scattering geometry: z(x,y)z.
The half widths of the optical phonons (at half-maximum) will be denoted by $\Gamma_a$ and $\Gamma_b$ below and above the peak, respectively. The total width $\Gamma = \Gamma_a + \Gamma_b$, and the asymmetry $\Gamma_a/\Gamma_b$ are plotted versus $x$ in Fig. 3. For the GaSb-like mode $\Gamma$ is an increasing function of $x$ until $x=0.75$, where the mode can no longer be detected. $\Gamma$ for the Ge-like mode rises first linearly with $(1-x)$, reaches a maximum for $x=0.35$ and then falls. The maximum values of $\Gamma$ (GaSb) and $\Gamma$ (Ge), 47 and 35 cm$^{-1}$ respectively, are close to those of the pure amorphous components (52 cm$^{-1}$ for a-GaSb and 47 cm$^{-1}$ for a-Ge). The asymmetry $\Gamma_a/\Gamma_b$ of the GaSb-like mode increases with $x$ until $x=0.25$. For $x>0.25$ $\Gamma_a/\Gamma_b$ decreases, whereas $\Gamma$ continues to increase. Similarly, the asymmetry of the Ge-like mode increases with $(1-x)$ until $(1-x)=0.20$. For $(1-x)>0.25$ the asymmetry decreases, whereas $\Gamma$ continues to increase, until $(1-x)=0.65$. This behavior is different from that found in the quasi-binary III-V alloys Ga$_{1-x}$Al$_x$As and Ga$_{1-x}$In$_x$As, where $\Gamma_a/\Gamma_b$ is an increasing function of $\Gamma$ (3) and in GaAs implanted with As$^+$ where $\Gamma_a/\Gamma_b$ and $\Gamma$ in samples that remain crystalline, are increasing functions of fluence (4). In these three systems $\Gamma$ was never greater than about 14 cm$^{-1}$, and the maximum value of $\Gamma_a/\Gamma_b$ was about 2.2.

By its very nature [Ga$_{1-x}$Ge$_x$] [Sb$_{1-x}$Ge$_x$] has more disorder than, say, GaSb$_{1-x}$As$_x$, since in the
present case both sublattices of the underlying lattice become disordered. The greater values of $r$ observed here are at least partly due to this effect. An important issue is whether the non-monotonic relation of $r_a/r_b$ to $r$ is simply due to the larger amount of disorder, rather than to qualitative changes in the nature of the disorder. The abrupt changes in $r_a/r_b$ (GaSb) near $x=0.20$ and $r_a/r_b$(Ge) near $x=0.80$ seem to occur over too small a change in $x$ to be simply a quantitative effect of disorder.

In references (3) and (4) the results were analyzed using the "Spatial correlation model" which introduces a correlation length $L$ to account for the wave-vector relaxation (5). The contribution of phonons of finite $q$ with frequency $w(q)$ and width $\Gamma_0$ is accounted for by use of the following expression for the Raman line-shape:

$$I(w) = \int \exp\left(\frac{-q^2 L^2}{4}\right) \frac{dq}{[w-w(q)]^2 + [\Gamma_0/2]^2}$$

(1)

$w(q)$ was taken to be that given by a linear chain model (3), (4). The resulting values of $r_a$, $r_b$, and $r_a/r_b$ are increasing functions of $L^{-1}$. A rough extrapolation of these results to large $r$, suggests that the $r$-values in Fig. 3 imply minimum values of $L$ of order $10^4$. When a more realistic model is used for $w(q)$, and when both TO and LO modes are included, it is possible that for very large $L^{-1} - 10^7$ cm$^{-1}$ Eq. (1) will give a line-shape with reduced asymmetry, but the change will not be an abrupt function of $L^{-1}$. The $r_a/r_b$ data (Fig. 3) suggest qualitative changes in the disorder at $x=0.20-0.30$ and $x=0.70-0.80$.

In (GaAs)$_{1-x}$Ge$_{2x}$, there is experimental and theoretical evidence for a transition from an average zincblende structure to an average diamond structure as $x$ increases past $x_c=0.35$ (6,7). X-ray diffraction data on (GaSb)$_{1-x}$Ge$_{2x}$ show a similar transition at $x_c=0.30$ (8). For $x>x_c$ there is no long-range zincblende order. The Raman results do not support the picture that site occupancy is completely random when $x>x_c$, because if that were the case we should see Raman scattering from Sb-Sb bonds. If these bonds were metallic, peaks should be seen at 115 cm$^{-1}$ and 150 cm$^{-1}$ (9). If the bonds were covalent, a peak would be seen at about 193 cm$^{-1}$ [a frequency slightly scaled down from the Raman frequency in gray tin (10)]. There are no sharp features near 115, 150,
or 190 cm\(^{-1}\) that could be identified with Sb-Sb bonds. This fact together with the observation that the GaSb-like phonon continues to exist up to \(x=0.75\) implies that Sb-Ga (and/or Sb-Ge) bonds exist, but not Sb-Sb bonds. If Sb-Ga bonds tend to be favored over Sb-Ge bonds, due to the coulomb interaction, there must be small regions of zincblende structure alternating with regions of anti-zincblende structure. The large values of \(L_1\) suggested by the large values of \(f\) imply that these regions would be as small as 10 Å in extent. This figure is consistent with our failure to see any microstructure using a scanning transmission electron microscope with a resolution of 50 Å.

Whatever the nature of the short-range order or microstructure, the \(\Gamma_a/\Gamma_b\) data suggest that the structure changes at \(x=0.20-0.30\) and again at \(x=0.70-0.80\).

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References

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