Alloying induced degradation of the absorption edge of InAs$_y$Sb$_{1-x}$

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InAs$_y$Sb$_{1-x}$ alloys show a strong bowing in the energy gap, the energy gap of the alloy can be less than the gap of the two parent compounds. We demonstrate that a consequence of this alloying is a systematic degradation in the sharpness of the absorption edge. The alloy disorder induced band-tail (Urbach tail) characteristics are quantitatively studied for InAs$_{0.05}$Sb$_{0.95}$.

It has long been noticed that the low energy tail region of the density of states of most, possibly all solids has an exponential character\[1][2]. Thus while one always observes an Urbach tail region in the optical spectra of even the high purity single crystals of III-V semiconducting compounds\[3][4][5], a significant band tailing has traditionally been associated only with amorphous\[6] or heavily doped semiconductors\[7][8]. In particular, the effects of alloying induced compositional disorder on the electronic states of the III-V semiconductors were generally considered benign. This long held view has undergone a major revision with the discovery of the nitride based semiconductor alloys, Ga$_{1-x}$In$_x$As$_{1-y}$N$_y$ and Ga$_{1-x}$In$_y$N. It has become evident that the process of alloying such “mismatched semiconductors”\[9] can lead to significant deviations from the virtual crystal picture, strongly changing the electronic and optical characteristics of the material. Mismatched alloys can typically be prepared only in dilute concentration due to the large size and electronegativity difference between the host and substituent atom. From the perspective of optical measurements, the compositional disorder leads to photoluminescence linewidths of many tens of meV, large Stokes’ shifts\[10][11][12] between the absorption and emission spectra and an absence of a sharp cut-off in the energy dependent transmission\[10].

In this paper we shall discuss the effect of alloying disorder on the absorption edge on InAs$_y$Sb$_{1-x}$. These alloys have disorder effects intermediate between the extremely incompatible GaAs$_{1-x}$N$_x$ and the completely miscible Ga$_{1-y}$Al$_y$As. A study of alloy disorder in these systems is particularly interesting because they allow for a close to equilibrium growth\[13] for a small value of $x$. GaAs$_{1-x}$N$_x$ alloys, on the other hand, are metastable configurations whose physical properties show a very strong dependence on sample history\[14]. From the technological point of view\[15][16][17], a few percent of InAs incorporation in InSb leads to a substantial lowering of the room temperature (RT) energy gap, to within the mid-infrared 8-12 $\mu$m transparent atmospheric window. This is significant because the energy gap of pure InSb—the III-V semiconductor with the smallest energy gap—is just outside this region. While previous studies\[18][14][20] have focused only on the energy gap of the system, alloying also leads to a broadened density of states and hence a smeared electronic distribution function. This may offset the advantage of the lowered energy gap.

**Experimental.**—Bulk InAs$_y$Sb$_{1-x}$ samples were grown by Rotatory Bridgmann method\[13] and the $\sim 5$ $\mu$m thick heteroepitaxial films on GaAs substrates were grown by liquid phase epitaxy\[21]. Since both these crystal growth methods operate close to equilibrium, the maximum arsenic incorporation was limited to around 5-6% if one chose to work with single-phase single-crystalline samples\[13]. The samples were comprehensively characterized for their structural\[13][21], optical\[19], transport\[22], and magnetotransport\[22] properties and the results indicated that these were among the best reported so far, with doping density less than $5 \times 10^{16}$cm$^{-3}$. Therefore, there is reason to believe that the absorption edge properties discussed

FIG. 1 RT transmission spectra for various InAs$_y$Sb$_{1-x}$ samples. Note that the desirable red shift in the transmission with increasing fraction of InAs is also systematically accompanied by broadening of the absorption edge.

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here result from a fundamental limitation of alloying. The optical transmission spectra were measured using a Fourier transform infrared spectrometer. The absorption coefficient $\kappa$ was calculated from the transmission $T$, using the well-known expression that accounts for multiple reflections within the sample, $T = (1 - R)^2 e^{-\kappa d}/[1 - R^2 e^{-2\kappa d}]$. Here $d$ is the thickness of the sample and $R = 0.4$ is the reflection coefficient, assumed to be constant in the spectral range of measurement. This equation is easily inverted by substituting $z = e^{-\kappa d}$ and then solving the quadratic equation in $z$.

The RT transmission from five InAs$_x$Sb$_{1-x}$ samples with progressively increasing value of $x$ is shown in Fig.1. We observe that the arsenide alloying induces the expected red-shift in the gap$^{[13,21]}$. It is also evident from Fig.1 that a larger arsenic alloying implies a progressive softening of the absorption edge, as the energy spread of the band-tail states grows with growing disorder.

To further investigate this band tailing, we shall focus on InAs$_{0.05}$Sb$_{0.95}$ sample which has the highest alloy composition among the bulk samples. Fig.2 shows the different parts of the absorption curve measured on InAs$_{0.05}$Sb$_{0.95}$. We can clearly distinguish three separate regions corresponding to (a) the band to band absorption$^{[17]}$ where the absorption coefficient $\kappa \propto [\hbar \nu - E_g(T)]^{1/2}$. Here $E_g(T)$ is the value of the energy gap at the given temperature $T$ and $\hbar \nu$ is the incident photon energy, (b) the Urbach edge absorption region where the absorption coefficient has an exponential dependence on energy (note the semilog scale in Fig.2), and (c) the free carrier absorption region$^{[10]}$ where the magnitude of the absorption curve increases with wavelength with a functional form that is dependent on the nature of scattering potentials$^{[23]}$.

Fig.3(a) highlights the behavior of the exponential Urbach edge portion of the absorption coefficient for bulk InAs$_{0.05}$Sb$_{0.95}$ at different temperatures between 300K and 433K. Different exponential curves when extrapolated to higher energies converge to a single point, the Urbach focus$^{[6]}$. Hence we observe that the well-known description of the Urbach edge developed for amorphous semiconductors seems to also describe the compositional disorder of mismatched III-V alloys. The exponential absorption coefficients measured at different temperatures can be phenomenologically described by the following single equation$^{[6]}$:

$$\kappa(\hbar \nu, T) = \kappa_0 \exp[(\hbar \nu - E_F)/E_U(T)], \quad (1)$$

with a temperature independent $\kappa_0$ and $E_F$. $E_U(T)$ in the above equation is the temperature dependent (inverse) slope of the exponential absorption coefficient and is a measure of the width of the Urbach tail. Henceforth, $E_U(T)$ will be referred to as the Urbach parameter.

Optical absorption occurs on a timescale much smaller than the typical phonon frequencies. One may therefore, in the Born-Oppenheimer spirit, argue that during a direct interband transition, an electron gets only a snapshot view of its surroundings and on this short time scale, the dynamically vibrating crystal is just a distorted arrangement of static ions$^{[1]}$. Thus in the context of optical absorption processes, thermal and structural disorders can be considered equivalent if the polaronic effects are small. The Urbach parameter is then expressed$^{[6]}$ as $E_U = X + Y(T)$, a simple addition of the thermal $[Y(T)]$ and temperature independent structural disorder $[X]$ components.

Fig.3(b) shows that the Urbach parameter is a monotonically increasing function of temperature. Furthermore, Fig.3(c), where we have plotted the relationship between the energy gap and the Urbach parameter, suggests a strong correlation between the temperature dependent changes in the two seemingly unrelated quantities. Therefore, the temperature dependent contribution is approximately estimated by assuming the same functional form for $Y(T)$ as that used to parameterize the change in the energy gap with temperature. One may$^{[6]}$, for example assume $Y(T) = Y_0/\exp(\theta/T) - 1$ or even, in our opinion, the Varshni type relationship, $Y(T) = Y_0T^2/[\theta + T]$. Using the Bose-Einstein type relationship, we get $[\text{Fig.3(b)}]$ the value of $\theta \approx 1850K$ and the disorder parameter $X \approx 35$meV. Note that the value of $\theta$ is not in agreement with what was earlier inferred for a much larger temperature range$^{[19]}$. This is because the linear relationship between the energy gap and the temperature dependence of the Urbach parameter is only approximate. In particular, the temperature dependent renormalization of the energy gap has a significant thermal expansion contribution that would not play any obvious role in changing the width of the Urbach tail. Thus although it is difficult to make physical sense of the quantity $\theta$, the fit does give an estimate of the disorder pa-

![FIG. 2 RT absorption spectrum for InAs$_{0.05}$Sb$_{0.95}$](image-url)
FIG. 3 (a) Urbach edge contribution to the absorption coefficient $\kappa$ at different temperatures for bulk InAs$_{0.05}$Sb$_{0.95}$. All the curves extrapolate to meet at a single point, denoted by the Urbach focus, $E_F$ at (225 meV, 250 cm$^{-1}$). (b) (squares) Temperature dependence of the slope of the Urbach edge measured between 303K and 433K. (solid line) Fit to the relationship described in the text, $\theta = 1850K$ and $X = 35$ meV (c) (circles) Relationship between the energy gap, $E_g(T)$ and the Urbach parameter, $E_U(T)$. The best straight line fit has a slope, $G = \Delta E_g/\Delta E_U = -1.55$

The inferred values of $X \sim 30$ meV and the RT Urbach parameter $E_U(300K) = 42$ meV are intermediate between that observed in high purity crystalline solids ($X < 10$meV) and that it amorphous materials ($X > 50$meV). Among the few other similar studies which exist for III-V semiconductor alloys, Reihlen, et al. [12] had measured the RT Urbach parameter of InP$_{1-x}$Sb$_x$ to be between 10meV at small and 50meV at larger alloy compositions. These results highlight the expected similarity of the two alloy systems. Studies on In$_x$Ga$_{1-x}$N alloys, on the other hand, have shown a much larger role of compositional disorder. Bayliss, et al. [10] found the RT Urbach parameter $E_U(300K)$ in In$_{0.2}$Ga$_{0.8}$N to be between 50 and 200 meV and Han, et al. [23] measured the same to be as large as 850 meV in In$_{0.13}$Ga$_{0.87}$N. Such large values may be attributed to the immiscibility of the two parent compounds [23]. Interestingly, the studies in Refs. [10] and [12] also correlate the Urbach parameter with the Stokes’ shift. For comparison, very heavily (10$^{19}$cm$^{-3}$) doped GaAs has an Urbach parameter of about 20meV at RT [8]. A value of about 90 meV was obtained for the structural disorder parameter in polycrystalline InN [20].

Finally, we shall discuss the physical interpretation of the Urbach focus. Following the theoretical analysis of Abe and Toyozawa, Cody [6] has suggested that the Urbach parameter, the Urbach focus and the energy gap, may be related by $E_g(T) = E_F + G E_U(T)$. Here $G = \Delta E_g/\Delta E_U$. A least squares fit to our data [Fig.3(c)] yields a slope $G = -1.55$, although the quality of fit is not very good. The value of the Urbach focus inferred from the above relation is found to be between 0.22 and 0.21 eV for measurements at different temperatures and is in reasonably good agreement with the convergence of the extrapolated exponential absorption spectra at 0.225 eV. The Urbach focus in amorphous semiconductors is identified as the effective direct energy gap of the (disorder-free hypothetical) virtual crystal [7]. This is both difficult to physically visualize, because of the topological disorder in real amorphous materials, and its value of 2.2 eV in amorphous silicon is not readily related to any other physically measured quantity in the system. The virtual crystal of a compositionally disordered solid, on the other hand, is much easier to visualize. Based on the above equation, one would expect the difference of the Urbach focus energy and the zero temperature gap of the real crystal to be equal to the disorder parameter responsible for the energy gap bowing [27]. But our inferred value of the Urbach focus, at about 0.22 eV, is closer to the zero temperature gap in this sample [19] itself, indicating that the above argument is at best qualitative.

Conclusions.—We have studied the optical absorption edge in crystalline InAs$_x$Sb$_{1-x}$ alloys grown by equilibrium technique. The absorption edge was found to be sensitive to the alloy composition, alloying led to a systematic broadening of the absorption edge. We further studied the Urbach edge’s contribution to the absorption coefficient in bulk InAs$_{0.05}$Sb$_{0.95}$ and found that the temperature dependent absorption coefficient curves could be extrapolated to a single point, the Urbach focus occurring at about 225 meV. The temperature dependence of the Urbach slope was modelled to infer a structural disorder energy of about 30meV for InAs$_{0.05}$Sb$_{0.95}$. As expected, this value is intermediate between what is observed in high quality compound semiconductors and heavily disordered amorphous solids. The universal nature of the Urbach edge suggests that the band tail disorder param-
eter can be used as a useful measure of sample quality, not just in amorphous solids but also in disordered III-V semiconductor alloys.

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