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Pressure coefficient of the direct band gap of $Al_xGa_{1-x}As$ from optical absorption measurements

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The shift with hydrostatic pressure of the absorption edge in $Al_xGa_{1-x}As$ compound semiconductors has been measured. The pressure coefficient of the direct-conduction-band minima dE_g^Γ/dP was obtained as a function of composition in the range $x = 0$ to 0.5. The pressure coefficient, when plotted againt the compositional parameter x, is found to increase up to $x = 0.25$ and then to decrease nonlinearly.

I. INTRODUCTION

Measurement of the shift in the optical absorption edge with hydrostatic pressure is a straightforward method to obtain the pressure variation of the energy gap dE_g/dP in a semiconductor. The method is particularly suited for semiconductors with direct band gaps since the optical absorption edge is then very well defined. The parameter dE_g/dP is very important for understanding the effect of pressure on the band structure of semiconductors, as well as interpreting transport property measurements.

Previous studies on group III-V compounds[1] have established the general nature of the shift of the three conduction band minima Γ, L, and X with hydrostatic pressure. In particular, dE_g^Γ/dP of GaAs has been studied by different methods with reasonable agreement between them.

In the present paper we report measurements of the pressure coefficient of the direct energy gap of $Al_xGa_{1-x}As$ as a function of the Al mole fraction x. When Al is substituted in the Ga sublattice, the ionicity of the compound changes. Moreover Al, unlike Ga, does not have d-core electrons. These circumstances may be expected to influence the value of dE_g^Γ/dP.

In this study we have investigated the dE_g^Γ/dP of $Al_xGa_{1-x}As$ compounds up to $x = 0.5$. Since the direct-indirect Γ-X band crossover occurs at $x = 0.45$,[2] the absorption edge becomes somewhat ill defined at higher values of x. The experiments and the results will be presented and discussed in this paper.

II. EXPERIMENTS

The high-pressure cell used was a Vascomax 300 steel vessel provided with sapphire windows on opposite sides.[3] The pressure cell was capable of reaching hydrostatic pressures up to 10 kbar. Plexol 262 was used as the pressure medium. A Spex Model 1500 spectrometer was used to record the absorption spectra. A tungsten lamp was found to be an adequate source of light to cover the spectral region of interest.

The $Al_xGa_{1-x}As$ samples were grown by the liquid-phase-epitaxy (LPE) technique on semi-insulating chromium-doped GaAs substrates. This structure precluded absorption studies in $Al_xGa_{1-x}As$, since the GaAs substrate has a lower energy gap than the $Al_xGa_{1-x}As$. This problem was overcome by selectively etching a circular area of GaAs substrate,[4] leaving the epitaxial $Al_xGa_{1-x}As$ layer intact for the light beam to pass through.

A typical sample was about 1 cm square with a layer of $Al_xGa_{1-x}As$ about 10 μm in thickness. The etched area was about 5 mm in diameter. Although the epilayers were thin, the unetched part of the GaAs substrate provided mechanical support. The sample was placed in a brass holder with a 3 mm opening. The holder was positioned in the pressure cell such that the optical beam passed through it centrally. All our measurements were made at room temperature. Absorption data were taken at pressure intervals of approximately 1–1.5 kbar. The optical absorption spectra were recorded 30 min after pressurization to equilibrate the temperature rise inside the pressure cell due to pumping.

III. RESULTS AND DISCUSSION

The data for two samples at $x = 0.15$ and $x = 0.5$ are shown in Figs. 1(a) and (b) as typical examples. The etched surface of the epilayers was not optically perfect and the transmission was quite diffuse. Hence the absorption data could not be presented in the conventional manner, namely, the absorption coefficient against photon energy. We have simply plotted the ratio I_0/I versus photon energy, where I is the transmitted intensity and I_0 is the intensity of the source. As pressure is increased the refractive index of the fluid changes and this affects the transmitted intensity. In processing the data necessary corrections were made for this effect from the refractive index data of Vedam.[5]

The application of hydrostatic pressure shifts the absorption edge to higher energies but the intensity-energy plots are parallel. From the set of parallel curves we extracted the pressure coefficient for the direct gap dE_g^Γ/dP for the different samples studied. These data are plotted against the compositional parameter x in Fig. 2. In the following table the data used in the plot are presented and the limits of errors are also given.

x	0	0.15	0.21	0.25	0.3	0.35	0.4	0.45	0.5
$\frac{dE_g^\Gamma}{dP}$ (10^{-6} eV bar^{-1})	11.4	11.8	12.0	12.2	10.8	10.25	10.2	10.0	10.1
Error (10^{-6} eV bar^{-1})	±0.1	±0.1	±0.2	±0.2	±0.1	±0.1	±0.1	±0.1	±0.1

The plot indicates that in the range of x from 0 to 0.25 the pressure coefficient dE_g^Γ/dP increases linearly from 11.4×10^{-6} eV/bar to 12.2×10^{-6} eV/bar, then drops to 10.2×10^{-6} eV/bar at $x=0.35$, and remains more or less constant at higher values of x.

It has been established that the value of the pressure coefficient of any energy band is determined basically by the symmetry of the band.[1,6] The perturbation effect of the core states (d states) depend in an inverse way on the ionization potential of the outermost d electrons.[7] In this connection it has been pointed out by Phillips[8] that in III-V semiconductors with the same anion the pressure coefficient varies inversely with the direct energy gap. Following his suggestion we have plotted in Fig. 3 dE_g^Γ/dP against E_g^Γ for the cases for which data are available. The value of E_g^Γ for AlSb is taken from Ref. 9, for GaAs and AlAs from Ref. 10, for all other materials from Ref. 1. The pressure coefficients of the direct band gaps can be found in Ref. 7. We have used here our value for the pressure coefficient of the direct band gap of GaAs.

Straight lines were drawn through the points corresponding to semiconductors with the same anion. The general trend is obvious. The line for Sb compounds has the highest values of dE_g^Γ/dP and also has the steepest slope. This can be explained by the fact that the ionization potential of the outer d electrons in Sb, the largest of all the three anions, is the least. For As compounds the dE_g^Γ/dP values are lower and correspondingly the slope is also smaller. For phosphorous compounds the lowest dE_g^Γ/dP values and the smallest slopes are seen. Among ma-

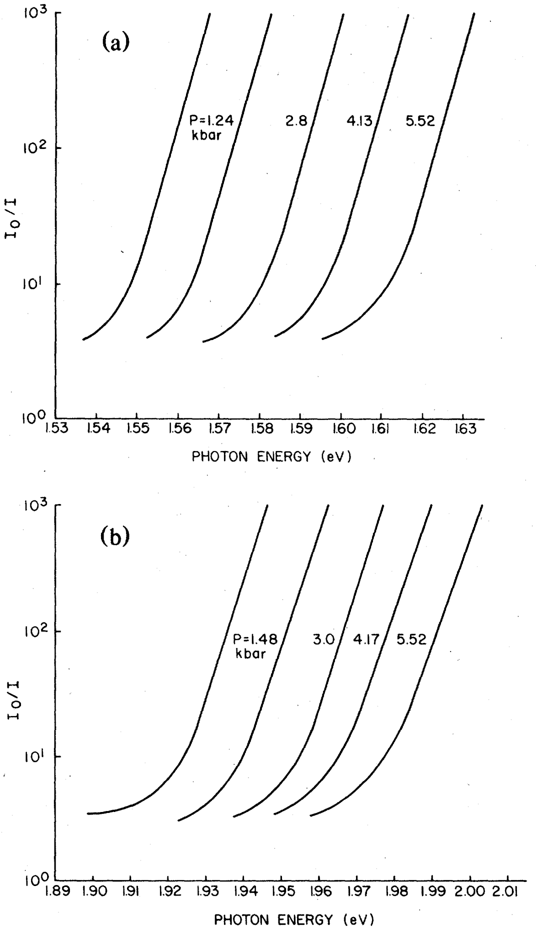

FIG. 1. Shift of the absorption edge with pressure in $Al_xGa_{1-x}As$. (a) $x=0.15$. (b) $x=0.5$.

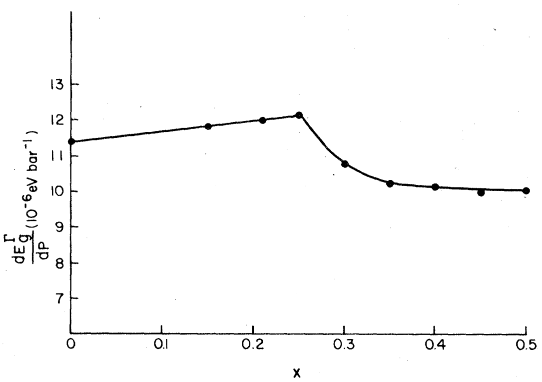

FIG. 2. Pressure coefficient of the direct band gap in $Al_xGa_{1-x}As$ as a function of the compositional parameter x.

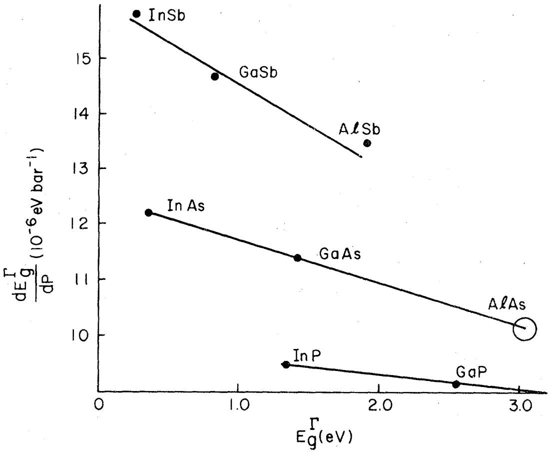

FIG. 3. Plot of the pressure coefficients of the direct band gap for a number of III-V compounds against the observed direct band gap. The straight line connects compounds with a common anion.

terials with the same anion the one containing In—the largest cation—has the largest pressure coefficient, followed by materials containing Ga and Al.

From the above empirical argument one would expect dE_g^Γ/dP for AlAs to lie within the area shown by the circle and the pressure coefficient of $Al_xGa_{1-x}As$ to be a smoothly decreasing function of x, since the direct gap in $Al_xGa_{1-x}As$ increases smoothly from 1.42 eV in GaAs to 3 eV in AlAs. However, the experimental data presented in Fig. 2 do not conform to these expectations. A sharp change in the pressure coefficient occurs in the range of x from 0.25 to 0.3 which is also the range of the percolation concentration of Al (the concentration at which the statistical probability of finding an Al having one or more Al neighbors is approaching unity) in $Al_xGa_{1-x}As$. We believe that this has some role to play. For instance, sharp changes in magnetic behavior in the Au-Fe system has been noted at the percolation concentration.[11] In our case it may be that at the percolation concentration a particular electronic character associated with the Ga $3d$ electrons begins to influence the system properties.

We note that these electrons nearly overlap the valence band[12] and may undergo a transition from a localized (Heitler-London) configuration to an itinerant (Bloch) state near this composition. This may modify the contribution of the D factor to E_0.[12] A transition of this kind would also be helpful in explaining other anomalies in comparing AlX and GaX (X = P,As,Sb) compounds such as relative heats of formation[12] and relative transition pressures to metallic phases.[13]

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