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Optical constants of $Ga_xIn_{1-x}P$ lattice matched to GaAs

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The optical constants of $Ga_{0.51}In_{0.49}P$ have been determined from 0.8 to 5.0 eV using variable-angle spectroscopic ellipsometry measurements at room temperature. The metal-organic vapor-phase-epitaxy-grown samples were x-ray analyzed to confirm lattice matching to the GaAs substrate. The effects of the native oxide were numerically removed from the data to determine the intrinsic optical constants. This is important because the optical constants reported become generally useful for modeling multiple-layer structures. A Kramers–Kronig analysis was used to reduce interference-related fluctuations in the below-gap refractive index. Near the band edge a mathematical form for excitonic absorption was included. Critical point energies were extracted using a numerical second-derivative fitting algorithm. © *1995 American Institute of Physics.*

I. INTRODUCTION

Because of the large band gap of $Ga_{0.51}In_{0.49}P$ lattice matched to GaAs, this material is promising for use in visible optoelectronics. $Ga_xIn_{1-x}P$ can be grown with high purity and excellent morphology by metal-organic vapor-phase epitaxy (MOVPE) using a wide choice of growth precursors over a wide range of compositions. We report in this article fully analyzed optical constants of GaInP lattice matched to GaAs. Variable-angle spectroscopic ellipsometry (VASE) was used, including numerical oxide layer removal, and Kramers–Kronig (KK) analysis to reduce the fluctuations of the refractive index in the below-band-gap region. We also determine ϵ_∞ from the full KK analysis, where ϵ_∞ means the dielectric function at frequencies sufficiently high that free-carrier effects are negligible.

II. THEORY

The complex reflectance ratio $\rho=R_p/R_s$, where R_p and R_s are the reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively, can be determined accurately by spectroscopic ellipsometry. The ratio has been traditionally defined as

$$\rho=\tan\Psi\exp(i\Delta), \tag{1a}$$

and is a function of Ψ and Δ, the amplitude and phase of the complex number. Results of ellipsometric measurements are often expressed as

$$\Psi_{ij}=\Psi(\hbar\omega_i,\Phi_j) \tag{1b}$$

and

$$\Delta_{ij}=\Delta(\hbar\omega_i,\Phi_j), \tag{1c}$$

where $\hbar\omega_i$ is the photon energy and Φ_j is the external angle of incidence relative to the sample normal. The pseudo-dielectric function $\langle\epsilon\rangle$ can be obtained from the ellipsometrically measured values of ρ_{ij}, based on a two-phase model (ambient/substrate),[1]

$$\langle\epsilon_{ij}\rangle=\epsilon_{1ij}+i^*\epsilon_{2ij}=\epsilon_a\left[\left(\frac{1-\rho_{ij}}{1+\rho_{ij}}\right)^2\sin^2\Phi_j\tan^2\Phi_j+\sin^2\Phi_j\right], \tag{2}$$

where ϵ_a is the dielectric function of the ambient and assumed to be constant. If the sample contains multiple layers (most samples have at least an oxide layer or surface roughness) the SE data must be numerically fit. For this purpose, a model must be assumed and Ψ_{ij}, and Δ_{ij} as in Eqs. (1b) and (1c) are generated and compared with measured data for the same wavelength and angle of incidence set. Ψ_{ij} and Δ_{ij} depend on a set of parameters, e.g., optical constants and thicknesses for each layer, interface qualities, surface properties, etc. The model should include all necessary characteristics to realistically simulate the behavior of the actual sample. A regression analysis is used to vary the model parameters until the generated and measured values match as closely as possible. This is done by minimizing the mean square error (MSE) function, defined as

$$\mathrm{MSE}=\frac{1}{2MN}\sum_{i,j}^{N,M}\left[\left(\frac{\Psi_{ij}-\Psi_{ij}^C}{\sigma_{ij}^\Psi}\right)^2+\left(\frac{\Delta_{ij}-\Delta_{ij}^C}{\sigma_{ij}^\Delta}\right)^2\right], \tag{3}$$

where i and j are indices for the wavelength and angle data sets, and the σ_{ij} are the standard deviations of the measurements. Note that one should know as much as possible about the physical structure of a sample since the regression analysis can potentially yield ambiguous results.

If a layer consists of an isotropic mixture of two materials a and b, with the microstructure much less then a

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fraction of the wavelength of light, then the macroscopic dielectric function can be described with the Bruggemann effective medium approximation (EMA),

$$f_a \frac{\epsilon_a - \epsilon}{\epsilon_a + 2\epsilon} + f_b \frac{\epsilon_b - \epsilon}{\epsilon_b + 2\epsilon} = 0, \tag{4}$$

where ϵ_a, ϵ_b, f_a, and f_b are the dielectric functions and the volume fractions of materials a and b, respectively.[2]

For the absorption spectra of semiconductors near the lowest direct band gap, it is well known that in addition to the atomic ionization continuum there are also broadened shoulders due to excitons. This can be described in simple form using coulomb forces, and a "dielectrically diluted" hydrogen atom model, where the binding energy is

$$\Delta E(\text{exc.})^{(n)} = -\frac{\mu}{8(h\epsilon_{dc}\epsilon_0)^2} \frac{1}{n^2} = \frac{\Delta E(\text{exc})^{(1)}}{n^2}, \quad n = 1,2,..., \tag{5}$$

and where μ is the reduced effective mass given by

$$\mu^{-1} = (m_e^{-1} + m_{hh}^{-1}). \tag{6}$$

ϵ_0, ϵ_{dc}, and h are the permittivity of free space, the static dielectric constant, and Planck's constant, respectively. An analytic expression of the above gap absorption for a semiconductor with the simple band model including excitonic effects is given by

$$\alpha(\hbar\omega) = -A \frac{2\pi\sqrt{|\Delta E(\text{exc})^{(1)}|}}{1 - \exp\{2\pi[|\Delta E(\text{exc})^{(1)}|/(\hbar\omega - E_G)]^{1/2}\}}, \tag{7}$$

where E_G is the band-gap energy and A an arbitrary amplitude.[3] Since the extinction coefficient k is related to the absorption coefficient by the relation

$$k(\omega) = \alpha \frac{c}{2\omega}, \tag{8}$$

where c is the velocity of light in vacuum, a relation for k including excitonic effects for the band edge can be found.

A detailed discussion of our VASE data and its analysis using this excitonic band edge model to smooth the fluctuations of the apparent refractive index below the band gap is presented in Sec. IV.

III. EXPERIMENT

Four samples of $Ga_{0.51}In_{0.49}P$ layers with nominal thicknesses of 1600 nm and GaAs buffer layers ~20 nm thick were epitaxially grown at 720 °C by MOVPE on liquid-encapsulated Czochralski GaAs substrates. The substrates were oriented along the [001] direction, with a tilt of 2° toward the [110] direction. The samples were grown under different partial In vapor pressures to obtain different misfit lattice constant values. Partial pressures [In/(In+Ga)] of 0.67, 0.66, 0.64, and 0.59 were recorded for the four samples. The corresponding perpendicular lattice mismatches, determined from x-ray measurements, were $\Delta a/a = +1\times10^{-4}$ (two samples), $+2\times10^{-4}$, and $+25\times10^{-4}$. VASE data, measured at room temperature, were taken on each sample at several angles of incidence and over the spectral range from E=0.8 to 5.0 eV.

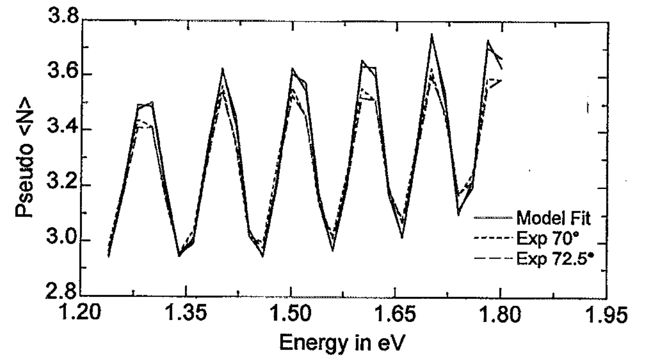

FIG. 1. Experimental and generated (best-fit) data for $\langle N \rangle$ using reference data for $Ga_{0.51}In_{0.49}P$ and oxide optical constants.

IV. RESULTS AND DISCUSSIONS

The two samples with the smallest perpendicular lattice mismatch ($\Delta a/a = +1\times10^{-4}$) were independently used to determine the optical constants of the $Ga_{0.51}In_{0.49}P$ layer and both results were found to be the same. First we assumed the refractive index N below the band gap, where k was set to zero, using Adachi's model for the optical constants of GaP and InP and linearly interpolating between all model parameters.[4] The oxide in the regression analysis was modeled using an appropriately weighted EMA of (51%) GaP oxide and (49%)InP oxide, using the method of Zollner to find the reference spectra for GaP oxide and InP oxide over a wide spectral range.[5]

The next step was to fit the generated data to the experimental data from 1.24 to 1.80 eV (below gap), using optical constants from Adachi's model and an oxide layer to determine the thicknesses of all layers (see Fig. 1). The generated values closely follow all oscillations in $\langle N \rangle$ which are due to multiple internal reflections. Thicknesses were obtained for the $Ga_{0.51}In_{0.49}P$ layer and the oxide layer, for both samples, as (1554.5±1.0) nm and (3.9±0.5) nm, (1540.7±1.5) nm and (4.4±0.8) nm, respectively. After fixing these thicknesses the optical constants for the $Ga_{0.51}In_{0.49}P$ layer were extracted over the entire measured range from 0.8 to 5.0 eV. Note that the thicknesses obtained in this procedure are dependent on the initially assumed below-gap optical constants, and that the subsequently determined optical constants, over the full spectral range, are dependent on these thicknesses. Therefore, this procedure should produce in the end virtually the same refractive index as initially assumed in the below-gap region.

Figure 2 shows the resulting N and k values. For comparison, the above-gap pseudovalues from Eq. (2) are also shown. Above the gap, the $Ga_{0.51}In_{0.49}P$ layer is optically thick, so the only difference between pseudo- and extracted values is the mathematical removal of the oxide layer in the latter. Note the large distorting effect that the overlayer has on the pseudovalues (the amount of distortion depends on the oxide thickness). The below-gap pseudovalues contain the

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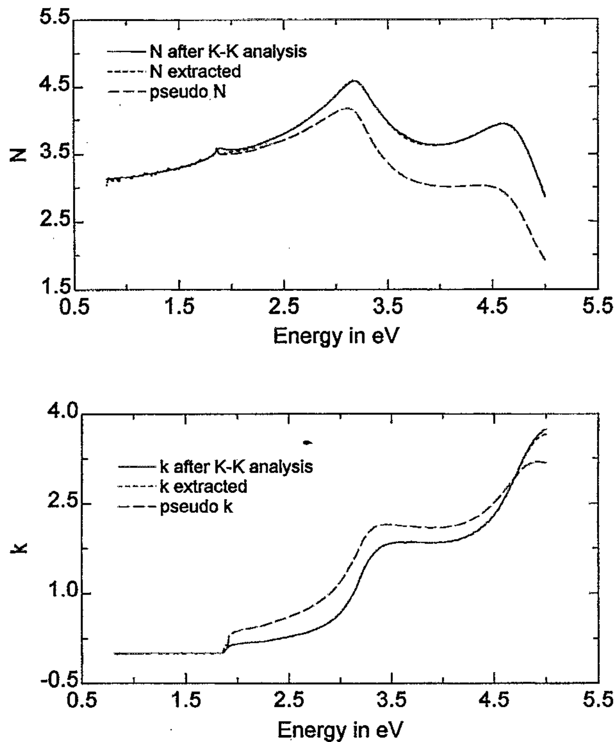

FIG. 2. Refractive index N and extinction coefficient k for $Ga_{0.51}In_{0.49}P$, $\Delta a/a = 1\times10^{-4}$, extracted directly from experimental data (short-dashed line) and after correction including KK analysis (solid line). Pseudovalues (long-dashed line) shown for comparison above the E_0 critical point.

interference oscillations shown in Fig. 1. For these reasons pseudovalues are not generally useful for modeling multiple-layer structures (though they may be adequate for determining critical point energies in a single layer, as in Ref. 11, if the oxide overlayer is not too thick).

Since the surface and also the interfaces of real systems are not ideal, one will always find deviations between generated and experimental values, especially below the band gap where the material is transparent and multiple reflections occur. Consequently many weak artificial oscillations appear in the transparent range of the extracted optical constants (Fig. 2). We used the following technique to correct the optical constants with knowledge of N and k above the band gap. We assume an excitonic model for the band edge for this material, using the analytic form from Eqs. (7) and (8). Thus, in the vicinity of the band edge,

$$k(\hbar\omega) = -A\,\frac{9.87\times10^{-6}}{\hbar\omega} \times \frac{2\pi\sqrt{|\Delta E(\mathrm{exc})^{(1)}|}}{1-\exp\{2\pi[|\Delta E(\mathrm{exc})^{(1)}|/(\hbar\omega - E_G)]^{1/2}\}}, \quad (9)$$

where all energies are expressed in eV. The values for the effective masses ($m_{hh}=0.63$, $m_e=0.12$) at the Γ point in the Brillouin zone and the static dielectric constant ($\epsilon_{dc}=11.75$) were taken from a simple interpolation between the values for GaP and InP.[6,7] Thus, only two parameters, A and E_G, were necessary to fit the analytical expression to the extracted values for the extinction coefficient. Note that the excitonic energy shift $|\Delta E(\mathrm{exc})^{(1)}|$ is less than 0.01 eV which is below our measurement resolution.

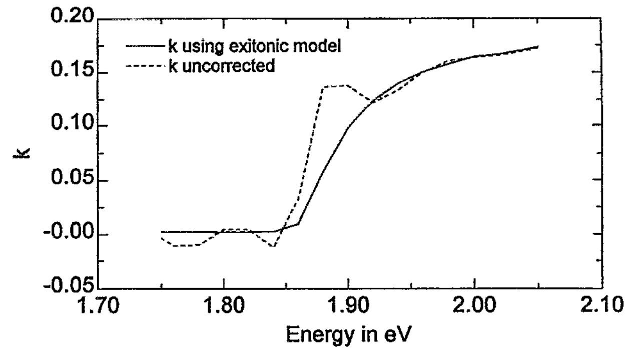

FIG. 3. K extracted from measured values (dashed line: same as short-dashed line of Fig. 2), and fit (solid line) of the excitonic band-edge absorption model to dashed line.

As a result of the fitting procedure (see Fig. 3) we observed a band-gap energy of $E_G = E_0 = 1.85\pm0.02$ eV and an amplitude of $(2.5\pm0.05)\times10^4$, which corresponds to an oscillator strength of roughly 5% for the excitonic transition if one compares these values to the quantum mechanically expressed excitonic absorption coefficient given by Wolfe, Holonyak, and Stillman.[8] In addition to the excitonic band-edge shape, we assumed that k is zero below the band-gap energy. The extinction coefficient spectra are then correct below and just above E_0 (up to 1.99 eV). Finally, we completed this spectral analysis at high energies by adding a fictitious oscillator to model the optical function above 5 eV. This controlled the numerically extracted values for N which were evaluated with a KK analysis over the entire spectral range. Note that N and k were transformed into the dielectric function format for this purpose. In Fig. 2, the original extracted and the KK calculated optical constants for $Ga_{0.51}In_{0.49}P$ are shown in the spectral range from 0.8 to 5.0 eV. Figure 4 shows the refractive index from 1.24 to 1.80 eV, before and after KK analysis, compared with the initial values for N assumed from Adachi's model. The final below-gap N values are very close to the initially assumed values, as expected.

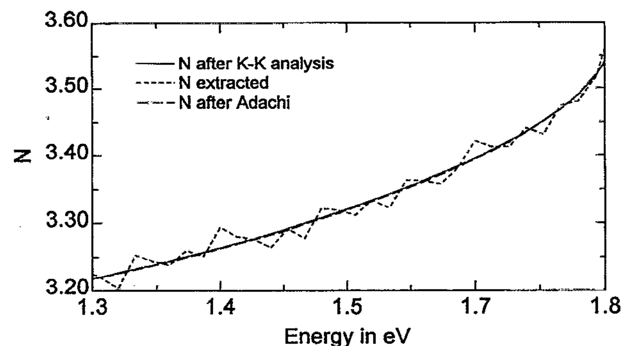

FIG. 4. Refractive index before (short-dashed line) and after (solid line) KK correction, compared with Adachi model (long-dashed line).

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TABLE I. Critical point energies from present work, compared with other published values, and with the binary end-point values.

Material	E_0 (eV)	E_1 (eV)	ϵ_∞
InP	1.35[a]	3.10[a]	9.61[b]
GaP	2.74[a]	3.70[a]	9.09[b]
$Ga_xIn_{1-x}P$	1.87±0.02[c]	3.21±0.02[c]	9.43±0.02[c]
	1.85[d]	3.243[g] (x=0.51)	9.34[h]
	1.86[e]		
	1.87[f]		
	1.947[g] (x=0.49)		

[a]Adachi (Ref. 4).
[b]Palik (Ref. 13).
[c]Present work (x=0.51); E_0 and E_1 from second-derivative line-shape analysis, ϵ_∞ from K analysis.
[d]Present work, excitonic band-edge fitting.
[e]Present work, photoluminescence (PL) measurement.
[f]Fouquet and co-workers (Ref. 13) results (x=0.50).
[g]Biswas *et al.* (Ref. 11) (gas-source molecular-beam epitaxy): E_0 from PL, E_1 from a straight-line formula fit to SE results (without oxide removal) over a range of x.
[h]Interpolation between GaP and InP (Ref. 13).

Excellent agreement between extracted and calculated refractive index was achieved. Note that ϵ_∞ was found from the KK analysis to be 9.43±0.03, which compares well with a linear interpolation between the ϵ_∞ values for GaP and InP.[13]

We have also determined the critical point energies using a numerical algorithm fitting to the smoothed second derivatives of the optical constants.[9,10] The results are shown in Table I, compared with values for GaP, InP, and results from earlier photoluminescence and ellipsometric measurements on $Ga_{0.51}In_{0.49}P$.[11,12] Note that only E_0 and E_1 were found here, and not $E_0+\Delta_0$ or $E_1+\Delta_1$, which are very weak components at room temperature. The E_0 found here is in good agreement with the result above for the excitonic band-edge fitting procedure. Photoluminescence measurement of E_0 also compares well with the ellipsometrically determined value for the same sample. Fouquet and co-workers studied the E_0 gap energies from partially ordered $Ga_{0.5}In_{0.5}P$ samples grown by metal-organic chemical-vapor deposition (MOCVD) at different temperatures. They found that the spectral position of the E_0 critical point transition determined by photoluminescence is very sensitive to growth conditions and varies from 1.86 to 1.99 eV.[12] Biswas *et al.* have determined E_1 by ellipsometric analysis of samples grown by gas-source molecular-beam epitaxy over a range of compositions.[11] Although they did not account for the oxide layer, this probably had little effect on the extracted E_1 values; reasonable agreement with our result is obtained for x=0.51.

V. SUMMARY

We have presented the optical constants of $Ga_{0.51}In_{0.49}P$ on GaAs grown by MOVPE, determined by VASE in the range of 0.8–5.0 eV at room temperature. They differ significantly from previously reported pseudovalues, in that the effects due to a native oxide overlayer were removed mathematically. A KK analysis and an excitonic band-edge absorption mathematical model were used to reduce the optical constants fluctuations in the below-gap region. Finally the E_0 and E_1 critical point energies were determined numerically using a smoothing derivative algorithm, for comparison with those from earlier work.

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