# Normal-incidence (001) second-harmonic generation in ordered $Ga_{0.5}In_{0.5}P$

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Despite their strong nonlinear susceptibility ($d_{14} \sim 120$ pm/V for GaAs), III–V zinc blende semiconductors do not show any second-harmonic generation in the [001] direction. We demonstrate that ordered GaInP does exhibit a nonvanishing second-order coefficient in this direction. We report second-harmonic generation parallel to [001] in ordered $Ga_{0.5}In_{0.5}P$ without domain mixture by transmission and reflection of a 1.42-$\mu$m fundamental beam in the transparency region of the material. The susceptibility tensor is fully characterized, and a value of $d_{22}'' \approx 13$ pm/V is measured along [001] for an ordering parameter $\eta = 0.43$. Susceptibility as a function of order parameter is investigated by reflected second-harmonic generation at the air–GaInP interface and interpreted in terms of bulk and surface contributions. © 2001 Optical Society of America

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Ordered semiconductors are alloys that have the same composition as the corresponding disordered semiconductors but have a specific arrangement of their constituent atoms that tends to form nearly pure atomic layers. This configuration induces a change in the crystal symmetry from the usual zinc blende for III–V semiconductors to CuPt type. In the past few years, attention has been focused on ordered $Ga_{0.52}In_{0.48}P$ because of the additional possibility for control of electronic and optical properties offered by CuPt type ordering.[1] Ordering induces, in particular, a controllable redshift of the bandgap energy that is predicted to be as high as 471 meV for the fully ordered material.[2] In practice, an order up to 0.54 has been reported[2] and appears to be the upper limit after growth temperature, substrate misorientation,[3] and V–III ratio optimization have been considered.[4]

Another fundamental aspect of second-harmonic generation is related to the symmetry of the crystal and concerns second-order optical nonlinearities. Indeed, the high $\overline{4}3m$ symmetry of III–V zinc blende semiconductors leads to the existence of only one nonlinear coefficient ($d_{14}$) for the second-order susceptibility tensor.[5] Though this coefficient is extremely large (120 pm/V for GaAs),[6] one important consequence of the symmetry rules is that second-order processes are forbidden along the three crystal axes [100], [010], and [001]. These axes are the common and widely used substrate orientations for mature epitaxy upon GaAs and InP. This vanishing susceptibility prevents any optoelectronic device grown upon (001) GaAs from working in a normal-incidence configuration (i.e., with fields propagating in the [001] direction) and from using the strong nonlinearity of GaAs. A solution consists of oblique-angle orientation of **what** the structures.[7,8] Another solution consists in growing **what** upon a disoriented GaAs substrate such as (111) ($d_{(111)} = 98$ pm/V) or (110) ($d_{(110)} = 120$ pm/V), but these growth methods are far less developed than growth upon (001) GaAs. In contrast to regular III–V semiconductors, ordered $Ga_{0.5}In_{0.5}P$ exhibits $3m$ symmetry. The lower symmetry in ordered GaInP is expected to lead to richer second-order susceptibility with four independent coefficients. As we show below, the lower symmetry *a priori* permits second-order processes in the [001] direction. Thus ordered GaInP appears to be a good candidate for normal-incidence operation of second-order nonlinearity–based devices.

Second-harmonic generation (SHG) in ordered GaInP has already been reported.[9,10] In the research reported in Ref. 9, the Maker-fringe measurement of $d_{14}'$ (110 pm/V) on wave guides gave an upper limit of 60 pm/V for $d_{33}'$ (coefficient in the Td frame of reference). However, the ordered sample exhibited domain mixing, which prevents any second-order nonlinear effect at normal incidence because of the spatial microscopic average of oriented susceptibilities. In Ref. 10, reflection SHG above the bandgap was reported and $3m$ symmetry of ordered GaInP was experimentally demonstrated. Singly resonant susceptibility of ordered GaInP was measured relative to the doubly resonant susceptibility of GaAs. We report here the direct measurement of normal-incidence SHG in the transparency region of ordered $Ga_{0.5}In_{0.5}P$ grown by widely used epitaxy upon (001) GaAs substrates and correlate order and susceptibility.

We grew the samples by low-pressure metal organic chemical-vapor deposition, using tertiary butyl phosphine as a phosphorus precursor. Domain mixture was prevented by use of a slightly misoriented, 3°-off-(001), GaAs substrate. The slight misorientation of the substrate from (001) toward (111)B permitted the growth of ordered $Ga_{0.5}In_{0.5}P$ without domain mixture.[3] In addition, the small misorientation was favorable for increasing the order parameter. The GaInP thickness was 400–700 nm, except for the sample studied in transmission (OR4455), which was a 1.6-$\mu$m-thick layer. Growth temperatures of

600–670 °C and various V–III ratios were investigated and yielded different order parameters $\eta$. Order $\eta$ was determined by bandgap measurement obtained by photoluminescence at room temperature. First the bandgap energy value was corrected to account for the exact composition and the small mismatch (measured by x-ray diffraction) between the $Ga_{0.5}In_{0.5}P$ and the GaAs layers. Order $\eta$ was then determined as in Ref. 2: The photoluminescence redshift with higher order was taken as a quadratic function[11] of $\eta$ with a total shift for a totally ordered structure of 471 meV. 1.913-eV room-temperature photoluminescence was assumed for a totally disordered structure.

In what follows, we consider the expression of the second-order susceptibility of ordered GaInP in the frame $[(110), (1\bar{1}0), (001)]$ that corresponds to cleaved edge facets and standard growth direction. The $d_{ij}$ matrix can be written as[9]

$$d_{ij}^{(O:\,wg)}$$

$$= \begin{bmatrix} 0 & 0 & 0 & 0 & \mathbf{d}_{14}' + \dfrac{d_{22}'' - d_{21}''}{2\sqrt{2}} & d_{16}'' \\[2mm] d_{21}'' & d_{22}'' & \dfrac{d_{22}'' + d_{21}'' - 2d_{16}''}{2} & -\mathbf{d}_{14}' + \dfrac{d_{22}'' - d_{21}''}{2\sqrt{2}} & 0 & 0 \\[2mm] \mathbf{d}_{14}' + \dfrac{d_{22}'' + d_{21}'' - 2d_{16}''}{2\sqrt{2}} & -\mathbf{d}_{14}' + \dfrac{d_{22}'' + d_{21}'' - 2d_{16}''}{2\sqrt{2}} & \dfrac{d_{22}''d_{21}'' + 2d_{16}''}{2\sqrt{2}} & \dfrac{d_{22}'' - d_{21}''}{2} & 0 & 0 \end{bmatrix},$$

where the primed and double-primed coefficients are univocally linearly related to the four independent coefficients in any other basis. The dotted boxes encapsulate the coefficients for a pump injected in the material along growth direction (001). In that case three coefficients, $d_{21}''$, $d_{22}''$, and $d_{16}''$, can participate in SHG. Note that the matrix of the disordered material is present through the $d_{14}'$ coefficient and is obtained by cancelation of the three other coefficients. Disordered GaInP therefore results in a forbidden normal-incidence SHG. Note also that ordered GaInP with domain mixing gives the same results because the mixing of domain orientation cancels the terms $d_{16}^{(O;wg)}$, $d_{21}^{(O;wg)}$, $d_{22}^{(O;wg)}$, $d_{23}^{(O;wg)}$, and $d_{34}^{(O;wg)}$, leaving the other components unchanged. Let $\alpha$ and $\beta$ be the polarization angles of the second-harmonic (SH) and of the pump, respectively, relative to the (110) axis. In what follows, we shall refer to a 0° angle as $s$ polarized and to 90° angle to as $p$ polarized. Then the dependence of the $p$ and $s$ components of the SH field on pump polarization angle $\beta$ of the fundamental field $E_\omega$ reads as

$$E_{2\omega}^{s} \propto d_{16}'' \sin(2\beta)E_\omega^{2},$$

$$E_{2\omega}^{p} \propto [d_{21}'' \cos^2(\beta) + d_{22}'' \sin^2(\beta)]E_\omega^{2}, \qquad (1)$$

where prefactors that correspond to propagation (transmission and reflection Fresnel factors, phase matching) have been dropped.

Copropagating SHG was performed on a suspended membrane of $GaInP_2$. The GaAs substrate of sample OR4455 (order $\eta = 0.43$) was removed, leaving an air–GaInP–air structure. The pump pulses, 130 fs long at 1.42 $\mu$m and emitted at a repetition rate of 82 Mhz, were focused onto the sample surface by a 8-cm focal-lens, leading to a spot diameter of 30 $\mu$m. The 60-mW average power corresponds to an intensity of ~600 MW/cm$^2$. The generated SH was filtered by a spectrometer and detected by a Si photodiode with standard lock-in techniques. The 1.42-$\mu$m wavelength of the pump pulses corresponded to a SH energy well below (78 meV) the bandgap in the transparency region of GaInP. The 1.6-$\mu$m thickness of the membrane corresponds approximately to 1.2$\times$ the coherent length of GaInP, which implies nearly optimal conversion efficiency.[12] The pump is injected at the small external angle of incidence of +10° chosen to compensate fully for the 3° misorientation of the substrate (assuming an index of refraction of 3.15 at 1.42 $\mu$m for $Ga_{0.5}In_{0.5}P$ and neglecting double refraction). The pump therefore propagates along (001) within the membrane. In what follows, we neglect the polarization dependence of Fresnel factors that originates from this very small angle of incidence.

Figure 1 shows the SH power transmitted by the OR4455 sample in $s$ (open circles) and $p$ (filled circles) polarization as a function of polarization $\beta$ of the pump. A strong SH is observed in $p$ polarization, whereas a small
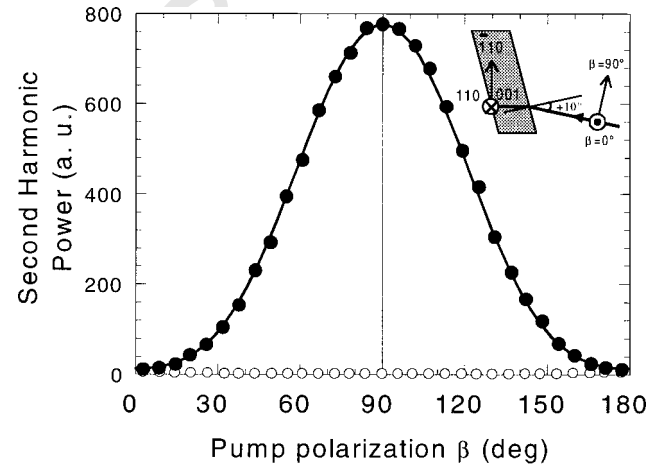


Fig. 1. SH power generated by transmission in the (001) direction through a 1.6-$\mu$m-thick ordered $Ga_{0.5}In_{0.5}P$ membrane for $s$ (open circles) and $p$ (filled circles) analyzer polarizations. The 130-fs pump spot diameter is ~30 $\mu$m, and its intensity is ~600 MW cm$^{-2}$. Solid curve, theoretical SH power dependence expected from the form of the susceptibility tensor [relations (1)]. Inset, the experimental configuration.

signal, 200 times smaller than in $p$, is recorded in $s$ polarization. The existence of strong SHG along [001] is a clear signature of the non-$\bar{4}3m$ symmetry of the crystal. More precisely, SHG results from the spatial average of the susceptibility of two phases, ordered and disordered, but only the ordered phase is involved along [001]. Assuming $3m$ symmetry, the dependence of the SH on pump polarization permits the relative determination of the nonlinear coefficients. The SH in $p$ has mainly a $\sin^4$ dependence, but a small cosine component is also present: The solid curve in Fig. 1 is the best fit of Eq. (1) to the experimental points with a ratio $|d_{21}''/d_{22}''| \approx 0.13$. The vanishing SH in $s$ then implies that $d_{16}'' \sim 0$ compared with $d_{22}''$.

To determine the absolute values of $d_{21}''$ and $d_{22}''$, we performed a SHG transmission experiment to ensure that there was a small angle of the propagating pump with the (001) axis.

When propagation along an axis misoriented from (001) by the small angle of $3°$ toward $(\bar{1}10)$ is assumed, the expression of the harmonic field reads as

$$E_{2\omega}{}^s \approx [-0.052d_{14}' + 0.0185(d_{21}'' - d_{22}'') + d_{16}'']$$
$$\times \sin(2\beta)E_{\omega}{}^2,$$

$$E_{2\omega}{}^p \approx [+0.052d_{14}' + 0.5d_{21}''$$
$$+ 0.46d_{22}'' + 0.036d_{16}'']E_{\omega}{}^2$$
$$+ [-0.104d_{14}' + 0.48(d_{21}'' - d_{12}'')$$
$$+ 0.0015d_{16}'']\cos(2\beta)E_{\omega}{}^2. \qquad (2)$$

Because of this small angle, the known $d_{14}'$ coefficient (110 pm/V; Ref. 9) is now projected onto the propagation direction and a significant fraction of $d_{14}'$ contributes to SHG.

Figure 2 shows the SH power generated in $s$ and $p$ polarization for internal angles of $3°$ and $6°$. One obtains this power by injecting the pump into the membrane at normal incidence and with a $10°$ angle of incidence toward $(\bar{1}10)$, respectively, for $s$ and $p$ polarization. The experiments were performed in identical conditions from one curve to another, and the power scale, although arbitrary, was always the same. The solid curves in Fig. 2 are the best fits to the four parameters $d_{14}'$, $d_{16}''$, $d_{21}''$, and $d_{22}''$ from Eq. (2) with the corresponding internal angles $3°$ and $6°$. Note that these fits correspond to a set of six equations that permit the determination of four coefficients. Nevertheless, only one set of coefficients reproduces all the curves (obvious sign symmetries are discarded). Assuming that $d_{14}' = 110$ pm/V, the relative values of the three other coefficients used in the solid curves are $d_{16}'' \approx -0.3$ pm/V, $d_{21}'' \approx -2.2$ pm/V, and $d_{21}'' \approx -12.7$ pm/V. There is no better fit to the experimental results than that which results from introducing a small nonvanishing value for $d_{16}$ and taking the relative signs of the four coefficients as proposed. $|d_{21}''/d_{22}'| = 0.17$ is slightly different from the value determined along (001), but it is worth noting that $d_{21}$ is much smaller than $d_{22}$ and that its determination is sensitive to

the exact power dependence of $\beta$. One should note that the $d_{ij}$ values are bound to be limited by partial order $\eta = 0.43$ of the sample.

We investigated SHG as a function of order parameter $\eta$. This systematic investigation was made with reflected SHG, directly upon the epitaxied surface of the samples at $0°$ incidence angle. The pump beam was focused upon the GaInP surface by a microscope objective and yielded an estimated spot diameter of 4 $\mu$m. The SH generated at the air–GaInP interface was collected by the same objective and directed to the grating spectrometer by reflection onto a dichroic blade. To remove from the signal the polarization dependence that originated from the dichroic blade, we corrected the system response and calibrated it with the SH generated at normal incidence by an (111)-oriented GaAs substrate ($d_{(111)} = 98$ pm/V). A representative pump polarization dependence of the reflected SH of GaInP is depicted in the inset of Fig. 3. Although relations (2) remain theoretically valid for the reflected SH,[13] the polarization dependence of the reflected SH is obviously not the same as the $3°$-off-transmitted SH shown in Fig. 2. This result suggests that reflected SH contains another component in addition to bulk susceptibility. The discrepancy between a reflected and a transmitted SH is attributed to the contribution of a surface SH generated at the interface between GaInP and air.[14] This nonnegligible contribution is at the origin of two features in the curves shown in the inset: the nonvanishing
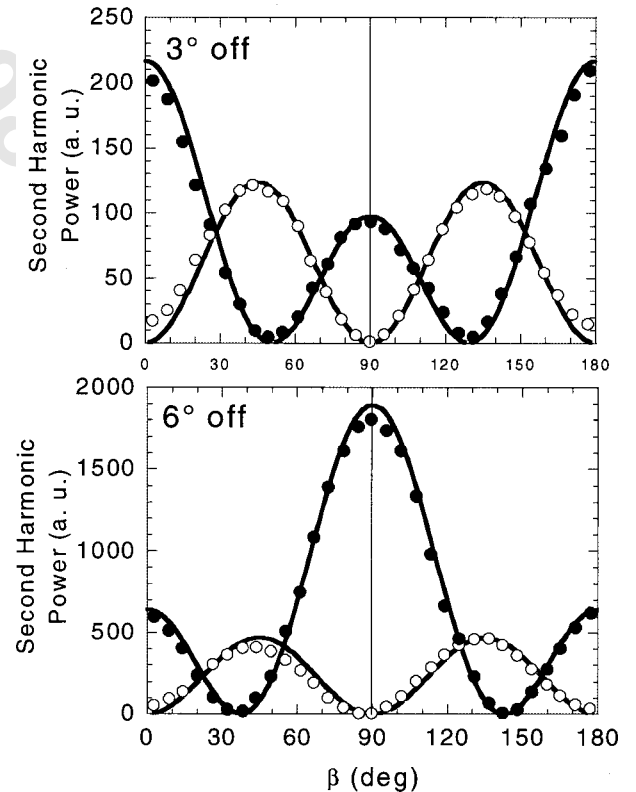
Fig. 2. Same as Fig. 1 but with $3°$ and $6°$ disorientation from (001) (external angles of incidence $0°$ and $-10°$, respectively). The scale is the same as in Fig. 1 and does not vary from one curve to another. Solid curves, best fits that correspond to the three ratios $d_{16}''/d_{14}' = -2.54 \times 10^{-3}$, $d_{21}''/d_{14}' = -0.0204$, and $d_{22}''/d_{14}' = -0.115$.
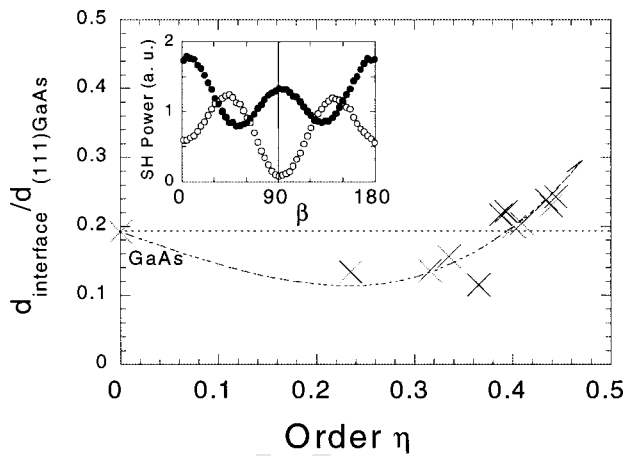
Fig. 3. Order dependence of the effective $d_{\text{interface}}$ coefficient (defined in the text) as a function of order parameter $\eta$ of partially ordered GaInP layers. The reference point at $\eta = 0$ corresponds to the measurement at 3°-off-(001) GaAs substrate. Dotted curves are guides for the eye. Inset, a typical $\beta$ dependence for the normal-incidence reflected SH power of ordered GaInP in $s$ (open circles) and $p$ (filled circles) polarizations. The intensity of the pump is estimated to be $\sim 35$ MW cm$^{-2}$.

SHG lowest value observed for $p$ polarization and the nonvanishing SHG value observed at $\beta = 0$ for $s$ polarization. Figure 3 shows the effective $d_{\text{interface}}$ coefficient extracted from the maximum power of the $p$-polarized reflected SH (square root of the power) for various samples as a function of order parameter $\eta$. As a reference, the normal-incidence $d_{\text{interface}}$ measured from a 3°-off-(001) GaAs substrate is shown at $\eta = 0$ ($d_{3°} = 19$ pm/V). Figure 3 clearly shows the dependence of susceptibility on order $\eta$. It is notable that $d_{\text{interface}}$ of weakly ordered GaInP ($\eta < 0.38$) can be smaller than that of the reference 3°-off-GaAs substrate, although the $d_{14}'$ coefficients of GaAs and GaInP are almost the same. This means that the bulk and surface $d_{ij}$ coefficients of ordered GaInP interfere coherently with $d_{14}'$ and contribute to decreasing the susceptibility that results from reflection on these slightly misoriented layers. Note that interference can also be constructive for $\eta > 0.38$ and leads to greater effective normal-incidence susceptibility than that of GaAs. This nonmonotonic dependence of SHG on order is in contrast to the monotonic dependence reported in Ref. 10 and again is attributed to effects of the surface susceptibility which in Ref. 10 are reported to be negligible.

In conclusion, second-harmonic generation has been demonstrated in the transparency region of ordered GaInP along the (001) direction (normal incidence).

Ga$_{0.5}$In$_{0.5}$P layers have been grown by metal organic chemical-vapor deposition 3°-off-(001) GaAs substrates to prevent domain mixture. Analyses of the polarization dependence of SH power have permitted determination of $d_{14}'$ relative to three other coefficients of the susceptibility tensor. Assuming a sensible $d_{14}' = 110$ pm/V, a susceptibility of $\sim 13$ pm/V is measured along (001) for an order of 0.43.

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