Optical constants and origin of the absorption edge of GaPN lattice-matched to Si

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We report the room-temperature dielectric function (DF) of GaPN grown lattice-matched on Si(100). Data were derived from spectroscopic ellipsometry measurements on a series of films prepared by metalorganic vapor phase epitaxy. The Kramers-Kronig analysis reveals good self-consistency between the real and the imaginary parts of the determined DF. The onset of a strong absorption in GaPN is clearly redshifted with respect to the direct band gap of GaP. In contrast, direct optical transitions at the E_0 and E_1 critical points (CPs) in GaPN are remarkably blueshifted. The experimental data near the absorption edge are analyzed using the $\mathbf{k} \cdot \mathbf{p}$ model of the valence-band structure and the experimentally motivated band anticrossing model to describe the conduction band. We found that the resulting Kane's matrix element for the lower conduction subband is quite small ($E_{P,-} = 0.64 \text{ eV}$), which indicates a relatively low probability of the respective direct optical transitions compared to typical direct band-gap semiconductors, such as GaAs, InP, or GaN. In addition, a considerable contribution of phonon-assisted optical absorption processes occurs. These observations are interpreted in terms of quasilocalization of nitrogen-induced electronic states responsible for optical transitions below the E_0 CP and their significant vibrational coupling to the lattice.

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I. INTRODUCTION

Lattice mismatch is an inherent problem when integrating classical III-V semiconductors with Si technology. Even GaP, which exhibits the smallest lattice mismatch to Si, allows for pseudomorphic growth of only several tens of nanometers. Incorporation of diluted concentrations of N into the host matrix is one option to reduce the lattice constant and, therefore, the lattice mismatch to silicon: For GaP, a replacement of approximately 2% of P by N is sufficient to yield the lattice match to Si at room temperature [1]. Moreover, such little amounts of incorporated N were found to drastically impact the electronic structure of the host, including a large redshift of the band-gap energy to values around 2 eV [2-4]. Such a reduced band gap is interesting in solar energy conversion for application in tandem structures as a top absorber layer combined with a Si bottom absorber [5]. Although quaternary GaPNAs compounds with even lower band gaps are considered for "pure" photovoltaic tandem devices [6], the higher band gap of GaPN could be more favorable for application in direct solar water splitting [7].

Regarding optoelectronic application, such as light exploitation, the type of the lowest band gap (direct or indirect) and the electronic band structure is essential: When, for instance, the absorber exhibits a direct band gap instead of an indirect one, its thickness can be reduced drastically, which saves material and at the same time requires shorter diffusion lengths and shorter minority charge carrier lifetimes, that is, the material is more tolerant to defects. Similar to GaAsN, the experimentally observed decrease in the band-gap energy

of GaPN can quantitatively be described within the band anticrossing model (BAC) [8,9] where the interaction of the conduction band (CB) of the host with the N level is accounted for by a nondiagonal element in the eigenvalue determinant causing a splitting of the CB. Nevertheless, considerable differences exist between GaP and GaAs regarding the impact of nitrogen incorporation on their optical properties. Specifically, whereas substitutional N incorporation produces a discrete energy level in the CB of GaAs [10], N atoms substituting P atoms cause several deep energy levels in the band gap of GaP due to clustering. In addition, unlike GaAs, GaP is an indirect semiconductor, which makes interpretations of experimental data more ambiguous. In early studies, a transition to a "directlike" GaPN band gap was suggested to occur already at N concentrations as little as 0.5% [11,12]. The nature of the band gap and the origin of the redshift, however, were objects of discussion: According to Kent and Zunger, N cluster states get energetically pinned, whereas the redshift of the band gap is caused by substitutional N incorporation perturbing the host states, and there is no "sharp transition" to a directlike band gap [13,14]. Zhang et al. [15] and Fluegel et al. [16], in contrast, attribute the redshift to a N impurity band [15,16].

Similar to other semiconductors, the basis for a detailed understanding of the electronic properties and possible applications of GaPN is its dielectric function (DF), $\varepsilon = \varepsilon_1 + i\varepsilon_2$. Reliable data for the DF of GaPN are, as yet, very scarce and not precise. There have been a few reports [17–19] on spectroscopic ellipsometry (SE) studies of films with N content (*x*) between 0 and approximately 0.04 grown on GaP substrates. In Ref. [17], only the pseudo-DF is presented, and only a qualitative indication of a considerable absorption tail (i.e., nonzero ε_2 values) below 3.0 eV has been provided. Buyanova *et al.* [18] as well as Kanaya *et al.* and Nakajima *et al.*

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[19] have reported that the magnitude and spectral shape of ε_2 in the low-energy range strongly depend on x, but a detailed quantitative analysis of the results has not been performed. In particular, the nature of the involved electronic transitions has not been studied in detail. An added complication is that films grown on GaP are strained, which significantly affects their optical properties and introduces some uncertainty into the derived data [17]. There have been no reports on the optical constants of GaPN films grown on Si substrates.

In this study, we grew state-of-the-art nearly unstrained GaPN layers on Si(100) substrates and performed roomtemperature SE measurements in the spectral range from 0.6 to 6.4 eV to derive the DF of GaPN lattice-matched to Si(100). Using a set of samples with different GaPN film thicknesses, we were able to derive accurate data not only in the range of high-energy critical points (CPs), but also below the E_0 CP, where the imaginary part of the DF is relatively low. The paper is organized as follows. Section II addresses the growth method, lattice parameters, crystalline quality of the studied samples, as well as details of SE measurements. Section III is concerned with the analysis of optical data. Special attention is paid to the determination of the thickness nonuniformity of the studied GaPN layers and quantification of the optical properties of their surfaces. In Sec. IV the derived optical constants of GaPN lattice-matched to Si are presented, and the self-consistency of the real and imaginary parts of the determined DF is investigated. Furthermore, the experimental data in the vicinity of the absorption edge are analyzed using the $\mathbf{k} \cdot \mathbf{p}$ model of the valence band (VB) structure and the BAC model to describe the dispersion in the CB. Section V is a brief summary of the main results of this study.

II. EXPERIMENT

A. Growth method and crystalline quality of the samples

GaPN was grown on Si(100) with 2° misorientation towards [011] by metalorganic vapor phase epitaxy (MOVPE) in a horizontal reactor (Aixtron AIX-200) using tertiarybutylphosphine (TBP), triethylgallium (TEGa), and dimethylhydrazine (UDMHy) as precursors in H₂ ambient at 50 mbar reactor pressure. The susceptor growth temperature was 650 °C. Prior to GaPN growth, the Si(100)-(1 \times 2) surface was prepared according to Ref. [20]. We applied a pulsed GaP nucleation consisting of ten alternating TBP, TEGa pulse pairs at 420°C/100 mbar [21] and heated to GaPN growth temperature under TBP stabilization. Low energy electron diffraction (LEED) patterns of such a roughly only 2-nm-thick nucleation layer showed no antiphase disorder [21]. We did not grow a thicker GaP buffer but continued with GaPN directly at a reactor pressure of 50 mbar at 650 °C. For all samples, Si preparation and GaP nucleation were identical, and the TBP:UDMHy ratio was adjusted to yield lattice matching to Si. The duration of the GaPN growth was varied such that four differently thick samples could be analyzed. After growth, the samples were cooled with TBP but without the UDMHy supply to prepare the group-V-rich surfaces [7]. Applying reflection anisotropy spectroscopy (RAS), the entire MOVPE growth was monitored in situ (Laytec EpiRAS) to guarantee well-defined and well-ordered surfaces throughout the process [7,20-22].

TABLE I. Root-mean-square surface roughness (δ_{AFM}) as well as film (*d*) and oxide overlayer (d_{ox}) thicknesses of the studied GaPN layers determined by AFM and spectroscopic ellipsometry analyses, respectively.

Sample	$\delta_{\rm AFM}~({\rm nm})$	<i>d</i> (nm)	$d_{\rm ox}$ (nm)
1	1.5	341.8 ± 0.02	1.40 ± 0.04
2	2.1	445.0 ± 0.02	1.55 ± 0.04
3	2.4	567.4 ± 0.02	1.37 ± 0.04
4	2.9	876.4 ± 0.03	1.62 ± 0.05

Ex situ, the samples were characterized with high-resolution x-ray diffraction (Bruker G8) and atomic force microscopy (AFM) in tapping mode (Bruker Dimension V) to obtain the N concentration in the bulk of the GaPN film and its rootmean-square (rms) surface roughness, respectively. Figure 1(a) shows the $\omega/2\theta$ diffractograms of the four GaPN/Si(001) samples measured around the [004] Bragg reflex of Si (plotted with an arbitrary intensity offset). The peak positions of the substrate and the film reflex are almost identical indicating nearly perfect lattice matching, which corresponds to an incorporation of about 2.1-2.2% of N into the GaP host matrix. With increasing film thickness, more GaPN is probed and the GaPN reflex becomes more intense as clearly visible on a logarithmic scale. The rms roughness values of the final GaPN/Si(100) surfaces were determined to be in the range of 1-3 nm (see Table I). Figure 1(b) shows an AFM image of the 342-nm-thick sample.

RAS measurements during growth showed GaPN surfaces with a $p(2 \times 2)/c(4 \times 2)$ surface reconstruction known from reference growth experiments of thinner layers [7] and modulated by Fabry-Pérot-like interference. During the RAS measurements, also the so-called dc detector voltage is measured, which corresponds to the reflectance convoluted with an (unknown) apparatus function. As displayed in Fig. 1(c), thickness-dependent oscillations occur during growth due to interference, and these are dampened due to absorption with increasing photon energy. The nearly constant mean "dc reflectance," that is no decrease in the envelope of the oscillations, indicates only little roughening of the surface during growth as is in line with the rms surface roughness values obtained by AFM.

B. Spectroscopic ellipsometry measurements

SE measurements were performed at room temperature in air on as-grown samples using a rotating analyzer Woollam VASE ellipsometer with an autoretarder. A 75-W short arc Xe lamp dispersed by a HS-190TM monochromator served as the light source. The spot size at normal incidence of light on a sample was ~2.5 mm in diameter. Standard "ellipsometry + depolarization" measurements were performed in the spectral range from 0.6 to 6.4 eV at three angles of incidence (60°, 66°, and 72°). The spectral resolution above and below a photon energy of 3.2 eV was 4 and 2.2 nm, respectively. The accuracy of the measured ellipsometric parameters Ψ and Δ was not worse than $\pm 0.03^{\circ}$ and $\pm 0.3^{\circ}$, respectively. For all investigated samples, the measured depolarization of light for photon energies below 3.8 eV did not exceed 0.1% being negligible within experimental accuracy. At photon energies



FIG. 1. (a) $\omega/2\theta$ diffractograms of the four GaPN/Si(001) samples measured around the [004] Bragg reflex of Si. Expected positions of relaxed Si(004) and GaP(004) are indicated by arrows, and the GaPN layer thickness as obtained by SE is given in the corresponding color. (b) AFM image (tapping mode) of the 342-nm-thick sample (10 × 10 μ m²). The rms value refers to the entire surface area shown. (c) *In situ* detector voltage (dc signal) during GaPN growth for three different photon energies.

above 3.8 eV, the measured depolarization remained low but was getting progressively noisy with increasing photon energy, mostly due to the limited sensitivity of the measuring setup. Therefore, it could not be evaluated reliably.

III. ANALYSIS OF OPTICAL DATA

Figure 2 shows Ψ and Δ spectra of the 876-nm-thick sample in a reduced energy region measured at an angle of incidence of 66° (solid lines) and simulated spectra (dotted lines) of an 880-nm-thick GaP layer on Si for comparison. The arrows in Fig. 2(a) indicate the direct band gap and the lowest indirect band gap of GaP at room temperature. They are placed at 2.780 and 2.275 eV, respectively [23]. At lower photon energies, GaP is transparent. It is seen from Fig. 2 that the GaPN material is transparent in the low-energy spectral range and its refractive index is similar to that of GaP. Significant absorption in GaPN occurs at approximately 2.0 eV, and it is considerably larger than that caused by the indirect transitions of GaP in the spectral range of 2–2.75 eV.

The spectral range below 2 eV where GaPN has a high transparency plays a decisive role in determining the optical model for the studied samples which then allows accurate and reliable optical constants of GaPN to be derived. Specifically, the following aspects should be emphasized.

(i) A possible thickness nonuniformity of the GaPN layers will result in a decreased magnitude of interference oscillations. Generally, in optical spectra this effect is hard to separate from that of a nonzero absorption. We measured SE spectra at several locations on the sample area of $\sim 8 \times 8 \text{ mm}^2$



FIG. 2. Spectroscopic ellipsometry spectra of the 876-nm-thick sample in a reduced energy range measured at an angle of incidence of 66° (solid lines) and calculated spectra (dotted lines) of an 880-nm-thick GaP layer on Si. The arrows indicate the direct band gap and the lowest indirect band gap of GaP.

resulting in a relative thickness nonuniformity of $(0.75 \pm 0.1)\%$ within the probing light spot and approximately identical for all studied samples. Simulations revealed that the observed thickness nonuniformity influences the depolarization of the reflected light well below 0.1%.

(ii) As mentioned in Sec. **IIB**, the measured depolarization of light in the low-energy spectral range is zero within experimental accuracy. Light-scattering effects due to possible nonidealities of the bulk and interfaces, thus, are negligible. In the following analysis, the interfaces Si/(GaP nucleation layer) and (GaP nucleation layer)/GaPN are assumed to be optically abrupt. Compared to early GaP growth on Si [24,25], the two-temperature MOVPE growth process [26,27] with pulsed nucleation and precursors used here is less prone to interfacial roughening. Moreover, we have shown previously that such thin GaP nucleation layers on Si already show the $(2 \times 2)/c(4 \times 2)$ surface reconstruction typical for MOVPE-prepared homoepitaxial GaP(100) surfaces [21]. LEED patterns verified the presence of only one surface domain indicating the absence of antiphase disorder [21], which we also showed for GaPN grown on Si(100) [7]. Recent density functional theory (DFT) calculations of the GaP/Si interface dielectric anisotropy [28] in comparison to that we observed experimentally [21,29] support the idea of an atomically well-ordered interface in contrast to intermixing over several monolayers [30]. DFT calculations also revealed that intermixing within more than one interfacial bilayer is energetically unfavorable [31].

(iii) Finally, the concept of an overlayer [32] is based on the well-known observation [32,33] that a thin transparent film (overlayer) on a semi-infinite transparent substrate leads to Δ values which can be significantly less than 180° (the angle of incidence is assumed to be below the Brewster angle). Figure 3 shows the simulated effect for a GaP oxide on a GaP substrate (a) and a (GaP oxide)/(GaP film)/(Si substrate) layered structure (b). For a nonzero oxide thickness, the spectrum as a whole is shifted to lower Δ values. The precise knowledge of d_{ox} is especially important for the accurate determination of the DF of GaPN in strongly absorptive spectral regions where the penetration depth of light is low and effects of surface nonidealities become relatively more significant.

The analysis of SE data was performed using the model (Si substrate)/(2 nm GaP nucleation layer)/(GaPN film)/overlayer/ambient. The optical constants of Si and GaP were taken from Ref. [34]. The overlayer was described by the dielectric function of anodically grown native oxide on GaP measured by Aspnes *et al.* [35] and parametrized by Zollner [36] as oxide overlayers with a thickness of several nanometers are usually assumed in studies of bulk GaP crystals [33,37,38] and GaP-based thin films [39,40].

To determine the optical constants of GaPN, SE data acquired from four studied samples were analyzed simultaneously assuming identical sample-independent optical properties of the GaPN material but individual overlayer thickness for each sample. It should be emphasized that involving samples with different film thicknesses (see Table I) into the simultaneous analysis and precise knowledge of overlayer properties are prerequisites for successful damping of possible artificial interference-related fluctuations in the determined optical constants below 3.0 eV. Considering the result of



FIG. 3. Calculated Δ spectra for (a) a GaP oxide layer on a GaP substrate and (b) a (GaP oxide)/(880-nm GaP film)/(Si substrate) layered structure.

independent measurements of the thickness nonuniformity of the GaPN layers addressed in (i), its value was not an adjustment parameter, but it was fixed at 0.75% for all samples. Then, the unknowns (adjusted parameters) to be determined from the analysis are the thicknesses of the GaPN film (d) and of the overlayer (d_{ox}) as well as the real and imaginary parts of the DF of GaPN.

In accordance with the foregoing qualitative discussion at the onset of this section, we adopted an iterative data analysis procedure in which the spectral regions of 0.6-1.8, 0.6-3.0 eV, and the entire measurement range from 0.6 to 6.4 eV are successively examined within each iteration. At the starting point, ε_2 and ε_1 values of GaPN are set to zero and to those of GaP, respectively, and approximate d and d_{ox} quantities are obtained by fitting the generated data to the experimental Ψ and Δ spectra in the low-energy range (0.6–1.8 eV). Then, ε_1 is allowed to vary as well. The next step is to analyze the extended photon energy range of 0.6-3.0 eV. First, d and d_{ox} are fixed, whereas ε_1 and ε_2 are varied. Then all four quantities are allowed to vary. At the last step, the thicknesses are fixed, and the real and imaginary parts of the DF of GaPN are extracted by a point-by-point analysis of the experimental SE data over the whole measurement range from 0.6 to 6.4 eV. The derived values of d, d_{ox} , ε_1 , and ε_2 are then used as the starting point for the next iteration. Several iterations were needed to accomplish good convergent results and a smooth merging of deduced ε_1 and ε_2 values of GaPN in the proximity of 1.8 and 3.0 eV. We observe that all SE spectra acquired from all studied samples are very well described by the determined DF which will be presented in Sec. IV A. The optically determined thicknesses of the GaPN films and of their overlayers are listed in Table I. The observed d_{ox} values agree well with the thickness of an



FIG. 4. The determined (a) real and imaginary parts of the dielectric function and (b) refractive index and absorption coefficient of GaPN lattice-matched to Si (solid lines). For comparison, data for GaP are presented by dotted lines. The inset in (b) shows the absorption coefficient at photon energies below 3.5 eV. (c,d) The same data over a reduced spectral range in the vicinity of the edge of strong absorption of GaPN and GaP indicated by vertically oriented filled and open arrows, respectively.

oxide overlayer typically found on air-exposed surfaces of GaP bulk crystals [33,37,38].

IV. RESULTS AND DISCUSSION

A. Dielectric function of a GaPN lattice matched to Si

Figures 4(a) and 4(b) present the determined DF of GaPN lattice-matched to Si (solid lines). For comparison, the DF of GaP is shown by dotted lines. Two dominant structures at about 3.7 and 5 eV are observed. The former is related to the E_1 CP, whereas four CPs in the range between 4.5 and 5.5 eV contribute to the high-energy structure [17,37]. It is seen from Figs. 4(a) and 4(b) that the E_1 optical transition in GaPN is blueshifted and has a significantly larger broadening compared to GaP. The structure at about 5 eV is also considerably broader than the respective structure of GaP. The increasing broadening of optical transitions in GaPN can be attributed to the alloy disorder [41–43] and the formation of N clusters [44,45].

From the derived DF, the refractive index (*n*) and the absorption coefficient (α) can be calculated. The inset in Fig. 4(b) presents an overview of the absorption coefficient at photon energies below 3.5 eV. It is seen that GaPN has a pronounced absorption edge at about 2.1 eV. Afterwards, in the range of 2.2–2.8 eV, the absorption coefficient levels at approximately 2×10^4 cm⁻¹; see also Fig. 4(d). At photon energies below 2 eV, the absorption coefficient decreases nearly exponentially. This can be related to optical transitions involving localized states of the band tails caused by compositional disorder and potential fluctuations [46].

Figures 4(c) and 4(d) show the real and imaginary parts of the DFs as well as the refractive indices and absorption coefficients of GaPN and GaP in a reduced spectral range near their edges of strong absorption which are indicated by vertically oriented filled and open arrows, respectively. At photon energies below approximately 3 eV, there is a close similarity between the real and the imaginary parts of the dielectric functions and the refractive index and absorption coefficient, respectively, as is expected for $\varepsilon_1 \gg \varepsilon_2$. Note that the absorption edge of GaP is considerably sharper than that of GaPN which indicates a significant broadening of optical transitions in the latter. It is also seen that in the spectral range of 2–2.75 eV, GaPN absorbs much stronger than GaP. However, in the range of $\sim(2.75-3.05 \text{ eV})$ its α and ε_2 values are lower compared to those of GaP. This provides the direct and unambiguous indication for a blueshift of the E_0 optical transition in GaPN. In Sec. IV C, this experimental observation will be discussed in more detail.

B. Kramers-Kronig consistency

In the present study, the Kramers-Kronig-consistency test of the real and imaginary parts of the determined DF of GaPN is performed in a way which is similar to that employed by Aspnes and Studna [32] for group IV and III–V semiconductors. Recently it has been applied to check the self-consistency of the anisotropic DFs of GaN [47]. The analysis procedure and its results are illustrated in Fig. 5. The expected contribution $\chi_{1,KK}(E)$ to the real part of the optical susceptibility χ (where $\varepsilon = 1 + \chi$), which originates from all optical transitions inside the measurement range, is obtained by calculating the Kramers-Kronig transform of the measured ε_2 spectrum,

$$\chi_{1,\text{KK}}(E) = (2/\pi) \mathscr{O} \int [z\varepsilon_2(z)/(z^2 - E^2)]dz, \quad (1)$$



FIG. 5. (a) Contribution $\chi_{1,KK}$ (dotted line) to the real part of the optical susceptibility originating from optical transitions inside the measurement range obtained by the Kramers-Kronig transform of the measured ε_2 . For comparison, the measured ε_1 spectrum is shown (solid line). (b) The difference $\varepsilon_1 - \chi_{1,KK}$ (thick solid line) and the calculated $1 + \chi_{1,os}$ spectrum (thick dotted line); it is hard to distinguish these two lines on the scale of (b); a slight deviation between them is visible only at the very high-energy end (6.1–6.4 eV) of the measurement range. he1 and he2 denote partial contributions due to two individual high-energy optical resonances outside the measurement range. (c) Inconsistency between the experimentally determined real and imaginary parts of the dielectric function of GaPN.

where the letter \mathscr{P} means the principal value of the integral and the integration is performed over the entire measurement range from 0.6 to 6.4 eV. The result is shown in Fig. 5(a) by the dotted line. For comparison, the measured $\varepsilon_1(E)$ spectrum is also shown by the solid line. The difference $\varepsilon_1(E) - \chi_{1,KK}(E)$ is shown by the thick solid line in Fig. 5(b). Its deviation from unity occurs exclusively due to absorption processes at photon energies lying outside the measurement range, i.e., below 0.6 eV (infrared active phonon modes) and above 6.4 eV (high-energy CPs) and, therefore, must be spectrally smooth [32]. The phonon contribution to the DF of GaPN at photon energies above 0.6 eV evaluated using parameters of the TO and LO phonons from Ref. [48] is found to be small and can be neglected within the experimental accuracy of this study. Like GaP [34], a relatively weak absorption is expected for GaPN in the range of 6.4–25 eV with ε_2 values being monotonically decreasing and nearly featureless. The effect of these high-energy optical transitions on the real part of the optical susceptibility in the measurement range was modeled by

$$\chi_{1,\text{os}} = \sum_{j} A_{j} E_{j}^{2} / (E_{j}^{2} - E^{2}), \qquad (2)$$

where j = he1 or he2 corresponds to two high-energy resonances, E_i is the respective resonance energy, and A_j is a dimensionless factor. The restriction for only two outside resonances he1 and he2 has a consequence that the model is not able to adequately describe the very high-energy end (6.1-6.4 eV) of the measurement range; see the thick dotted line $(1 + \chi_{1,os})$ in Fig. 5(b). Of course, the analysis can be extended up to 6.4 eV by including further high-energy resonances and/or applying a more realistic description of the ε_2 spectrum above 6.4 eV. However, this does not substantially change the results for inconsistencies between the measured ε_1 and ε_2 spectra at lower photon energies. Therefore, the modeling was restricted to two outside resonances, and the corresponding A_i and E_i values were found by the best match of the calculated $1 + \chi_{1,os}$ spectrum to the $\varepsilon_1 - \chi_{1,KK}$ spectrum in the reduced photon energy range of 0.6–6.0 eV. The fitting curve is indicated in Fig. 5(b) by the thick dotted line. The respective contributions of individual high-energy resonances are shown by lines denoted as he1 and he2.

Figure 5(c) shows the relative difference $[(1 + \chi_{1,KK} + \chi_{1,os}) - \varepsilon_1]/\varepsilon_2^{max} \times 100\%$ which represents the inconsistency [32] between the experimentally determined real and imaginary parts of the DF. Here, ε_2^{max} is the peak value in the measured ε_2 spectrum (approximately 26.8 at 5.0 eV). It can be concluded that the measured ordinary ε_1 and ε_2 spectra show overall good self-consistency within $\pm 0.5\%$.

C. Analysis of the absorption edge

For many direct-band-gap binary compound semiconductors, band structure parameters are well known from numerous independent studies. This allows calculation of $\varepsilon_{2,v}(E)$ spectra due to band-to-band optical transitions between an individual valence band v and the lowest conduction band without any further assumptions [49]. One method to calculate the spectra is based on the $\mathbf{k} \cdot \mathbf{p}$ model of the VB band structure in the vicinity of the Γ point. In this case, the VB structure and transition probabilities from the heavy-hole (hh), light-hole (lh) and split-off-hole (sh) VBs into the CB are calculated using Luttinger parameters (γ_1 , γ_2 , γ_3) and the spin-orbit splitting (Δ_{so}) by solving the 6×6 Hamiltonian for eigenvalues and eigenfunctions. Excitonic effects are described in the effectivemass approximation within the framework of Elliott's model [50]. It has been shown that very good agreement with roomtemperature experimental ε_2 spectra can be achieved provided that the nonparabolicity of the CB is taken into account and the excitonic contribution is weighted with the help of a phenomenological weighting factor f_x which is temperature and material dependent [49]. It has also been observed that, in addition to discrete excitons ($\varepsilon_{2,DX}$), a sideband ($\varepsilon_{2,PSB}$)

anti-Stokes shifted to higher photon energies may occur in ε_2 spectra. Such a band is especially well pronounced in wurtzite GaN and ZnO and is explained by a strong coupling between excitons and LO phonons in these materials, which allows optical absorption processes where a photon simultaneously creates an exciton and several phonons [51]. The resulting expression for the imaginary part of the DF has the following form [51,52]:

$$\varepsilon_2(E) = f_x \varepsilon_{2,\text{DX}} + \sum_v \left[1 + f_x (S_v - 1)\right] \varepsilon_{2,v} + \varepsilon_{2,\text{PSB}}, \quad (3)$$

where the summation in the second term runs over the three VBs (v = hh, lh, sh), S_v is the VB-specific Sommerfeld (or Coulomb enhancement) factor, and the first, second, and third terms represent contributions of discrete excitons (DXs), Coulomb-enhanced band-to-band (CBB) transitions, and phonon-assisted optical processes [multiphonon sideband (PSB)], respectively. An explicit presentation of the above model for ε_2 , calculation procedures, and results for binary III-V and II-VI compound semiconductors can be found elsewhere [49,51-53]. Here, we apply it to GaPN for which a phenomenological description of the CB dispersion based on the two-level band anticrossing model was proposed [9,11]. According to the BAC model, the presence of isoelectronic N atoms substituting P atoms leads to the splitting of the original CB $E_{c}(\mathbf{k})$ of GaP at the Γ point into two subbands, E_{-} and E_+ [11],

$$E_{\pm}(\mathbf{k}) = \frac{1}{2} \Big\{ [E_{\rm c}(\mathbf{k}) + E_{\rm L}] \pm \sqrt{[E_{\rm c}(\mathbf{k}) - E_{\rm L}]^2 + 4V_0^2 x} \Big\}, \quad (4)$$

where **k** is the wave vector of the conduction-band electrons, $E_{\rm L}$ is the energy of the localized states introduced by the substitutional N atoms, V_0 is the coupling parameter, and x is the N content (x = 0.021 for the samples studied in this study). Based on previous results for GaP and other binary zinc-blende semiconductors which included also the nonparabolicity of the lowest CB [49,53], we calculate $E_c(\mathbf{k})$ as follows:

$$E_{\rm c}(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m_0} (1+C^*) + \frac{E_{\rm g}}{2} + \frac{E_{\rm g}}{2} \bigg[1 + \frac{4E_{\rm P}}{3E_{\rm g}} \bigg(\frac{2}{E_{\rm g}} + \frac{1}{E_{\rm g} + \Delta_{\rm so}} \bigg) \frac{\hbar^2 \mathbf{k}^2}{2m_0} \bigg]^{1/2}, \quad (5)$$
$$\frac{1}{m_{\rm e0}^*} = 1 + C^* + \frac{E_{\rm P}}{3} \bigg(\frac{2}{E_{\rm g}} + \frac{1}{E_{\rm g} + \Delta_{\rm so}} \bigg), \quad (6)$$

where \hbar is the Planck constant, m_0 is the free-electron mass, E_g is the direct band gap of GaP ($E_g = 2.78 \text{ eV}$ [23]), E_P is the momentum (Kane's) matrix element in energy units ($E_P = 25 \text{ eV}$ [49]), C^* takes into account effects of remote conduction bands, and m_{e0}^* is the electron effective mass at the CB bottom of GaP in units of the free-electron mass ($m_{e0}^* = 0.125$ [49]). The energies in Eqs. (4)–(6) are counted from the top of the hh VB, and all above-mentioned quantities are given for the room temperature. Possible nitrogen-induced changes in valence band states in the vicinity of the Γ point are largely unknown [54]. To describe the VB structure of GaPN lattice-matched to Si, in the following analysis we adopted a set of $\gamma_1 = 4.05$, $\gamma_2 = 0.49$, $\gamma_3 = 1.25$, and $\Delta_{so} = 0.08 \text{ eV}$ recommended for GaP [23,55]. The resulting



FIG. 6. (a) Conduction band (E_-, E_+) and valence band (hh, lh, and sh) dispersions of the GaPN lattice-matched to Si. The valence band is anisotropic. k_{001} and k_{011} are magnitudes of the wave vector in the ΓX and ΓK directions of the Brillouin zone, respectively. The conduction band is assumed to be isotropic. For comparison, the conduction-band dispersion of GaP is shown by the dotted line. Note a discontinuity of the energy axis. (b) Wave-vector dependence of the electron effective mass in the E_- and E_+ conduction subbands of GaPN (solid lines) and in the conduction band of GaP (broken line).

VBs are nonparabolic and anisotropic as can be seen from Fig. 6(a).

An iterative procedure was used to adjust the model expressed by Eqs. (3)–(6) to experimental ε_2 data of GaPN in the range of 1.8–3.2 eV. Within the BAC model, quantities of $E_{\rm L}$ and V_0 unambiguously determine the electron energy and effective mass in both the E_{-} and the E_{+} subbands at an arbitrary **k** as illustrated in Fig. 6. The wave-vector-dependent electron effective mass $m_{\pm}(\mathbf{k})$ shown in Fig. 6(b) is defined by $\hbar^2 \mathbf{k}^2 / [2m_0 m_{\pm}(\mathbf{k})] = [E_{\pm}(\mathbf{k}) - E_{\pm}|_{\mathbf{k}=0}]$. Then, the effective

Rydberg energy R_{\pm} for both subbands is calculated by [49] $R_{\pm} = (\mu_0 m_0 e^4)/[2(4\pi \varepsilon_0 \varepsilon_s \hbar)^2]$, where $1/\mu_0 = 1/(m_{\pm}|_{\mathbf{k}=0}) + \gamma_1$, *e* is the free-electron charge, ε_0 is the electric constant, and ε_s is the static dielectric constant. The latter was assumed to be identical to that of GaP ($\varepsilon_s = 11.1$ [49]). Values of the weighting factor f_x for the E_- and E_+ subbands were estimated to be approximately 0.94 and 0.82, respectively, based on a linear interpolation between GaN (where $f_x = 0.97$ [51]) and GaP ($f_x = 0.8$ [49]) using the Rydberg energy as the interpolation basis.

Simulations showed that it is impossible to achieve satisfactory agreement with the experimental ε_2 data of GaPN without considering the contribution of phonon-assisted optical processes expressed by the third term in Eq. (3). Within the framework of the effective-mass approximation, the excitons are treated as being made up of an electron from the CB and a hole from each one of the highest VBs. Then, two different exciton series can be formed in zinc-blende semiconductors [49]. The first series is fourfold degenerate and originates from the hh and lh VBs. The second series is twofold degenerate and originates from the sh VB. Accordingly, also two different PSBs may occur. However, the measured ε_2 spectra of GaPN indicate a quite large broadening of optical transitions (see below), whereas the value of Δ_{so} (0.08 eV) is comparably small. As a result, different exciton and PSB series are not resolved in the measured spectra, and in the following only the summed contributions due to all discrete excitons and all phonon sidebands are shown for each one of the E_{-} and E_{+} subbands which will be called the zero-phonon line (ZPL) and the PSB, respectively. The latter was modeled as the sum of multiphonon (N = 1, 2, 3, ...) replicas of the ZPL scaled by a factor of $f_0 b^{N-1}$ and anti-Stokes shifted to higher energies by $N(\hbar\omega_{\rm LO})$, where $\hbar\omega_{\rm LO}$ is the LO-phonon energy $(\hbar\omega_{\rm LO} = 50.7 \,{\rm meV}$ for GaPN [48]) and f_0 is the contribution of the N = 1 (one-phonon) state normalized to that of the ZPL. For the meaning of b and more details of the modeling, see Refs. [51,52]. Hence, the adjustment parameters were $E_{\rm L}$, V_0 , two Kane's matrix elements $E_{P,\pm}$ for the E_+ and E_- subbands, respectively, the broadening parameter σ , and values of f_0 and b that describe the PSB for the E_{-} subband. The E_{+} subband is quite similar to the original CB of GaP (see Fig. 6) and, as expected, the contribution of phonon-assisted processes was found to be small. However, it could not be unambiguously quantified by the fitting procedure and in order to minimize the number of adjusted parameters, f_0 and b values for the E_+ subband were fixed at those characteristic of moderately doped GaN [52]. The adjustment parameters and some other specific quantities of the E_{-} and E_{+} subbands determined from the analysis are listed in Table II.

The best matching for the measured ε_2 values of GaPN in the range between 1.8 and 3.2 eV is shown in Fig. 7(a) by the thick solid line. It corresponds to $E_L = 2.25$ and $V_0 = 1.98$ eV. Whereas the E_L value is similar to those previously reported (2.18 eV from photomodulated transmission at 300 K [11], 2.32 eV from photoluminescence excitation (PLE) at 2 K [56], 2.25 eV from a combination of temperature-dependent optical transmission, PLE and SE measurements [18], and 2.21 eV from photocurrent and electroluminescence measurements of GaPN light-emitting diodes at 300 K [57]), the determined V_0 value is considerably less than 3.05 eV [11], 2.7 eV [56], TABLE II. Parameters of the E_{-} and E_{+} subbands determined from the analysis of the experimental ε_2 data: Rydberg energy, direct band gap, electron effective mass at the band bottom in units of the free-electron mass, Kane's matrix element, and parameters of the multiphonon sideband.

	E_{-} subband	E_+ subband
Rydberg energy (meV)	21	11
Direct band gap (eV)	2.12	2.90
Electron effective mass	0.77	0.15
Kane's matrix element (eV)	0.64	29
f_0	5.3	0.2
b	0.65	0.3

2.76 eV [18], and 4.38 eV [57] found in the above-referenced experiments and slightly higher than 1.69–1.74 eV calculated by the tight-binding method [45]. Concerning experiments, it is quite evident that their conclusions are strongly sensitive to the details of the data analysis, specifically, whether or not excitonic effects, Stokes shift, details of the electronic structure, broadening of optical transitions, etc., are properly included.

Thin solid lines denoted by E_+ [Fig. 7(a)] and E_- [Fig. 7(b)] represent individual contributions of the respective subbands. Broken lines are their decomposition into partial contributions of different mechanisms as discussed above. For the E_+ subband, the multiphonon sideband has a small magnitude and, therefore, is not shown in Fig. 7(a). It can be seen that the Coulomb-enhanced band-to-band transitions dominate



FIG. 7. (a) Best matching curve (thick solid line) for the measured ε_2 values of GaPN (circles) in the range between 1.8 and 3.2 eV and individual contributions of the (a) E_+ and (b) E_- subbands (thin solid lines). Broken lines are the decomposition into partial contributions of different mechanisms: CBB, ZPL, and PSB.

for both E_{-} and E_{+} subbands. However, in case of the E_{-} subband, also the PSB makes a significant contribution. Its integrated intensity is approximately 15 times larger than that of the ZPL. There is also a significant broadening of optical transitions. It was incorporated into the calculated $\varepsilon_2(E)$ spectra using the Gaussian line-shape function. We assumed the broadening to be identical for all optical transitions and found $\sigma = 0.078 \,\mathrm{eV}$ which results in a full width at the half maximum (FWHM) of 0.26 eV. The determined Kane's matrix element for the E_{-} subband ($E_{P,-} = 0.64 \text{ eV}$) is very small compared to the E_+ subband of GaPN ($E_{P,+} = 29 \text{ eV}$; see Table II) or to typical direct band-gap semiconductors, such as GaAs and InP, for which the optically determined E_P is 27.6 and 21.2 eV [53], respectively, or wurtzite GaN, where the Kane's matrix element amounts to 18.8 and 21.0 eV [51] for the ordinary and extraordinary light waves, respectively. This indicates a much lower probability of direct optical transitions involving electronic states of the E_{-} subband. It is also noticeable that the room-temperature photoluminescence (PL) of these samples demonstrates a broad nearly featureless band with the FWHM and the PL peak energy of approximately 0.2 and 1.95 eV, respectively. An adequate PL analysis of corresponding GaPN films requires a detailed time- and temperature-dependent PL examination and needs to be the subject of a separate upcoming study.

Broad absorption and emission bands showing qualitatively similar properties (i.e., large FWHMs and Stokes shifts as well as relatively low external quantum efficiencies) have been observed in studies of optical transitions via deep-level defects in many semiconductors; see, e.g., Refs. [58,59] for a 0.8-eV PL band in AlGaAs and Refs. [60,61] for blue, green, and vellow PL bands in GaN. Most frequently, this behavior is described using the concept of a one-dimensional configuration coordinate diagram with large Huang-Rhys factors of the participating ground and excited electronic states being obtained. This indicates a strong localization of the states and their strong coupling to the lattice vibrations meaning that a large number of phonon modes, both extended and local, accompany an optical transition [58-61]. Recently [62], first-principles calculations of PL line shapes for deep-level defects in GaN and ZnO have been presented which confirm these empirical findings. It has also been observed that heavy doping drastically enhances the phonon-assisted optical absorption in GaN [52].

Arguing by analogy, we conclude that all peculiar features of the E_{-} subband of GaPN lattice-matched to Si revealed by our analysis can be explained in terms of considerable localization (quasilocalization) of the corresponding nitrogeninduced states and their significant vibrational coupling to the lattice. This is the main reason for the small value of the determined Kane's matrix element of the E_{-} subband. It seems, therefore, that GaPN material is not suitable for the production of highly efficient light-emitting devices, such as those based on AlGaInP and InAlGaN compound semiconductors [63]. One can assume that in the range of 2.0–2.8 eV the degree of localization is monotonically decreasing as the photon energy is increased and, therefore, the transition probability is monotonically increasing. This effect is not included into our analysis. In addition, the wide energy distribution of the low-energy N-related states due to alloy fluctuations and nitrogen clusters can play an important role in defining the spectrum, broadening, and probability of optical transitions.

A final remark addresses the appearance of a plateau in the measured ε_2 spectrum at photon energies between 2.3 and 2.8 eV [see Fig. 7(a)]. Based on pseudopotential supercell calculations, Dudiy *et al.* have attributed a similar plateau observed in photoluminescence excitation spectra of GaPN to "sizable nitrogen-induced changes of the valence band states well below the band maximum" [54]. Our analysis shows that the plateau in the range of 2.3–2.8 eV results mostly from the combined effect of the phonon-assisted and Coulomb-enhanced band-to-band transitions [see Fig. 7(b)]. Whereas the contribution of the former transitions decreases as the photon energy is increased, the contribution of the CBB transitions increases. The latter is directly related to the large and wave-vector-dependent electron effective mass in the $E_$ subband [see Table II and Fig. 7(b)].

V. CONCLUSION

We determined the DF of a state-of-the art nearly unstrained GaPN lattice-matched to Si(100) in the spectral range from 0.6 to 6.4 eV at room temperature. The Kramers-Kronig analysis revealed that the real and imaginary parts of the determined DF are self-consistent within $\pm 0.5\%$. The experimental data near the absorption edge were analyzed using the $\mathbf{k} \cdot \mathbf{p}$ model of the valence-band structure and the empirically motivated band anticrossing model to describe the conduction band. The determined Kane's matrix element for the lower conduction subband is small $(E_{P,-} = 0.64 \text{ eV})$ which means that the probability of the respective direct optical transitions is quite low compared to typical direct band-gap semiconductors, such as GaAs, InP, or GaN. In addition, we found that phonon-assisted optical absorption processes make a considerable contribution to the optical response at photon energies below the E_0 critical point. These observations were interpreted in terms of the quasilocalization of the nitrogen-induced electronic states responsible for the redshifted optical absorption of GaPN lattice-matched to Si and their significant vibrational coupling to the lattice.

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a set of $\gamma_1 = 4.05$, $\gamma_2 = 0.49$, and $\gamma_3 = 1.25$ is adopted which is also mentioned in Ref. [22] (Sec. III D) as a set of Luttinger parameters being in good agreement with cyclotron resonance experiments and acceptor binding energies.

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