Temperature induced giant shift of phonon energy in epitaxial boron nitride layers

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Abstract
The recent progress in the growth of large-area boron nitride epilayers opens up new possibilities for future applications. However, it remains largely unclear how weakly attached two-dimensional BN layers interact with their substrate and how their properties are influenced by defects. In this work, we investigate hBN layers grown by metal organic vapor phase epitaxy using Fourier-transform infrared spectroscopy in the temperature range of 160–540 K. Our measurements reveal strong differences in the character of layer-substrate interaction for as-grown and delaminated epitaxial layers. A much weaker interaction of as-grown layers is explained by wrinkles formation that reduces strain at the layer-substrate interface, which for layers transferred to other substrates occurs only in a limited temperature range. The most striking result is the observation of a giant increase in the $E_{1u}$ phonon energy of up to $\sim 6$ cm$^{-1}$ in a narrow temperature range. We show that the amplitude and temperature range of the anomaly is strongly modified by UV light illumination. The observed giant effect is explained in terms of strain generation resulting from charge redistribution between shallow traps and different defects, which can be interpreted as a result of strong electron-phonon coupling in hBN. The observed narrow temperature range of the anomaly indicates that the effect may be further enhanced for example by electrostrictive effects, expected for sp$^2$ boron nitride.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Hexagonal boron nitride (hBN) is a wide bandgap layered material [1] with strong sp$^2$ covalent bonds in-plane and weak van der Waals bonds between adjacent layers [2]. An additional asset of hBN is the high thermal and chemical stability [3–6]. These properties make hBN an important component in many novel van der Waals heterostructures [7–10] or as an encapsulating layer that increases the durability of other less durable materials such as perovskites [11] or transition metal dichalcogenides [12, 13].

However, the effective usage of many systems and microdevices in everyday life is dependent on the possibility to be scaled up. The solution for this problem are epitaxial techniques which enable few-inch area layer growth. In case of hBN the structural and optical quality of the epitaxial layers is still inferior to those of better-studied flakes exfoliated from the bulk crystal. The difference between epitaxial and bulk hBN is also observed in the interaction with other materials [14, 15]. Hence, in order to combine epitaxial hBN layers with other materials it is important to understand the different properties of defects in epitaxial hBN and the mechanisms of their creation as well as the rules that govern interactions between epitaxial hBN and other materials.

One of the most popular optical characterization methods is Raman spectroscopy. However, epitaxial layers often exhibit
intensive defect-related photoluminescence that hinders the observation of a Raman signal, making the spectra difficult to analyze properly. Here, we use a complementary method, which is Fourier-transform infrared (FTIR) spectroscopy. This method is free of disturbing photoluminescence contribution and moreover allows us to obtain precise information (e.g. concerning the thickness, as we will demonstrate) from the characteristic peak intensity. In this work, we present $E_{1u}$ hBN phonon energy-temperature dependences measured with FTIR spectroscopy. We measured delaminated and as-grown epitaxial layers. For as-grown samples characteristic wrinkles are created during cooling after growth, because of the relaxation of the accumulated strain energy caused by the negative thermal expansion coefficient of hBN [16]. We revealed that the layer-substrate interaction is almost completely reduced for as-grown layers, as they behave almost like bulk material. We ascribe this behavior to be a consequence of wrinkles creation. In addition, we observe an anomalous, giant upshift of phonon energy that occurs in a narrow temperature range. This effect is explained in terms of charge redistribution of hBN defects. The observed effects highlight that defects in hBN play not only an important role for electrical conductivity, mid-gap photoluminescence or single photon emission, but can also strongly affect the phonon modes in a complex manner.

2. Methods

2.1. Samples

The boron nitride samples used in this work were obtained with metal organic vapor phase epitaxy (MOVPE) using an Aixtron CCS 3 × 2" system. Two inch sapphire wafers were used as substrates, and ammonia and triethylboron (TEB) were used as precursors of nitrogen and boron, respectively. In most processes, hydrogen was used as a carrier gas, but a few samples were obtained using a nitrogen atmosphere. Thin epitaxial boron nitride samples (from atomic monolayer to 70 nm), oriented parallel to the sapphire surface, were obtained by three growth regimes: continuous flow growth [17, 18], flow modulation epitaxy [18, 19] and two-stage epitaxy [20]. Due to a pre-growth nitridation step a thin AlN layer is formed at the sapphire interface. For measurements, we prepared $\sim 8 \times 8$ mm pieces of investigated hBN layers. We are aware that our samples may consist of boron and nitrogen atoms bonded with $sp^3$ bonding in different phases such as hexagonal (hBN), rhombohedral (rBN), turbostratic (tBN), Bernal stacking (bBN) [20, 21]. However, to simplify the notation in the present work, we will use hBN having in mind all layered boron nitride phases.

For temperature-dependent FTIR measurements, we chose a 41 nm thick hBN layer grown in Flow Modulation Epitaxy regime and a 20 nm thick hBN layer grown in Two-stage Epitaxy regime. The growth parameters for both samples are available in the supplementary materials. The thicker layer was also delaminated and deposited onto a new sapphire substrate to obtain information about the layer-substrate interaction. The delamination procedure is already described in the literature [18, 22].

2.2. Experimental details

X-ray measurements were performed using a Panalytical Xpert diffractometer equipped with a Cu sealed x-ray tube and a parallel beam Bragg x-ray mirror. For all samples, x-ray reflectometry (XRR) measurements were taken (ω/2θ scans). To obtain the thickness of the hBN layer from the XRR measurements, the PANalytical X’Pert Reflectivity software package was used. This program makes use of the recursive Parratt formalism for reflectivity [23–25]. In the fitting procedure, the thickness, density, and roughness of the hBN and AlN layers were taken into account, as well as the roughness of the sapphire substrate. It should be pointed out that in the calculations only a one-dimensional model is considered.

A Thermo Scientific Nicolet Continuum Infrared Microscope with a 32× Schwarzschild infinity corrected objective (NA 0.65) was used for FTIR reflection measurements. All samples presented were measured at 3 points approximately 3 mm apart with an illuminated area of $70 \times 70 \mu m$. The spectra were collected in the range of 650–4000 cm$^{-1}$ with a resolution of 0.964 cm$^{-1}$ for samples thinner than 4 nm and 0.482 cm$^{-1}$ for the rest of the samples. The light beam was perpendicular to the surface of the sample.

A Linkam THMS350EV cryostat was used for temperature dependence measurements. The real temperature value was measured with a thermocouple soldered to the sample surface with indium. The calibration allowed for a range of possible temperatures between 157 and 538 K. Before each temperature-dependent measurement, the sample was measured at room temperature on six different locations to be sure that the sample is isotropic.

For UV sample irradiation, we used an EQ-99X LDLS lamp emitting light in the range 170–2500 nm.

2.3. Characterization method

To characterize hBN layers, we simulate the whole FTIR spectrum. To do so, we assume that the material is a medium composed of harmonic damped oscillators. This allows us to introduce dynamic dielectric function (DDF). In the function there are parameters such as oscillator self-energy $\omega_0$ and its damping parameter $\gamma$ which provide us with information about the phonon properties in the material. In our analysis method, we consider a thin layer on a thick substrate, also described by its DDF. It is possible because of the phase difference analysis that comes from the interference of light beams reflecting on the subsequent interfaces. This method allows to obtain information about the thickness of the layer $d$ and interface roughness $\sigma$ considered for $d > 100$ nm. All the details about the characterization method are available in the supplementary materials.

In figure 1 we present an exemplary spectrum modelling for three different samples. The samples were grown using three different growth conditions that resulted in different material properties (i.e. strain, amount of defects, thickness). The modelling works well for each of the samples. The values of the modelled parameters are presented in table 1. The peak position at about 1367 cm$^{-1}$ corresponds to the $E_{1u}$ phonon mode of $sp^3$ hybridized boron nitride [26]. The high quality of
our epitaxial samples is manifested by the values of the $\gamma_{BN}$ parameter for the $E_{1u}$ mode, which are similar to the values of the Raman $E_{2g}$ peak width for high-quality epitaxial layers reported by other groups [18, 27–29]. The IR-active mode is nearly degenerated with the $E_{2g}$ Raman-active mode and decays with the same channels [30]. An experimental relation of the width (connected with $\gamma_{BN}$) of the FTIR spectra and the $E_{2g}$ Raman modes for our epitaxial samples is presented in the supplementary materials. The inset in figure 1 shows that the $E_{1u}$ peak intensity directly depends on the thickness of hBN. The high reflectivity below 1000 cm$^{-1}$ is connected to the presence of sapphire substrate [31]. One can see that the modeled curves in figure 1 describe experimental data almost entirely. All important features of the spectrum are reproduced and the values in table 1 are very precisely determined with relative error values $\approx$ 0.01% for $\omega_{BN}$ and $\approx$ 1% for $\gamma_{BN}$ and $d_{BN}$. This precision enables to detect smallest deviations in strain, quality and thickness of epitaxial layers.

The principal advantage of the described method over the very basic peak Lorentzian fitting is the access to the physical properties of the sample, even if the sample structure is complex. The absorption shape modified by the damping parameter $\gamma$ which influences the peak position or layer thickness is out of range for simple fitting. The thickness results coming from our method are in very good agreement with the results obtained with XRR for the samples in the range 2–70 nm (see supplementary materials figure S1).

The method can be applied for samples in the thickness range from a single atomic layer to several $\mu$m (see supplementary materials figure S2).

### 3. Results and discussion

Since the phonon energy is a good indicator for strain [28], we investigated as-grown and delaminated samples. Due to the delamination process, both samples should exhibit different layer-substrate interactions. The origin of the interactions is that the layer is locally pinned to the substrate as a result of the point defects present and the disorder on the interface during nucleation at the initial stage of the growth process [28]. Then after the growth process, when the temperature is decreased, the hBN layer expands while the substrate shrinks, which is the result of the opposite sign of the thermal expansion coefficient for both materials. As we provided a reliable method for the identification of the phonon energy of hBN, it is possible to analyze the temperature dependencies of the lattice vibrations of the epitaxial layers $\omega_{BN}(T)$. As we present in figure 2, the phonon energy for as-grown and delaminated layers follows different trends. To be able to extract information about layer-substrate interactions, we need to know what influences this $\omega_{BN}(T)$ dependency. It is governed by 4 dominant factors: the undisturbed phonon energy at 0 K $\omega_0$, the lattice constant change (thermal expansion) $\Delta\omega_L$, the anharmonic phonon decay $\Delta\omega_{AN}$, the layer-substrate interaction $\Delta\omega_S$ caused by the difference in thermal expansion coefficients of layer and substrate:

$$\omega_{BN}(T) = \omega_0 + \Delta\omega_L(T) + \Delta\omega_{AN}(T) + \Delta\omega_S(T).$$  \hfill (1)

Taking the hBN thermal expansion coefficient provided by Yates et al [16], and using it for the density functional theory (DFT) calculations as presented by Casco et al [32], one can obtain the energy change due to the thermal expansion coefficient:

$$\Delta\omega_L(T) = -2.347 + 2.137 \times 10^{-2}T - 1.177 \times 10^{-5}T^2.$$  \hfill (2)

According to DFT calculations, the $E_{1u}$ phonon has two dominant decay paths: three-phonon process and four-phonon process [30]. Both give the following contribution to $\Delta\omega_{AN}$ [33]:

$$\Delta\omega_{AN}(T) = A\left(1 + \frac{1}{e^{\theta_1/T} - 1} + \frac{1}{e^{\theta_2/T} - 1} + \frac{1}{e^{\theta_3/T} - 1} + \frac{1}{e^{\theta_4/T} - 1} + \frac{2}{e^{\theta_5/T} - 1} + \frac{2}{e^{\theta_6/T} - 1} + \frac{2}{e^{\theta_7/T} - 1} \right)$$

$$+ B\left(1 + \frac{2}{e^{\theta_1/T} - 1} + \frac{2}{e^{\theta_2/T} - 1} + \frac{2}{e^{\theta_3/T} - 1} \right)$$

$$+ \frac{2}{e^{\theta_1/T} - 1} + \frac{2}{e^{\theta_2/T} - 1} + \frac{2}{e^{\theta_3/T} - 1} + \frac{2}{e^{\theta_4/T} - 1} + \frac{2}{e^{\theta_5/T} - 1} + \frac{2}{e^{\theta_6/T} - 1} + \frac{2}{e^{\theta_7/T} - 1} \right),$$  \hfill (3)

where $A, B$—constants that are related to three- and four-phonon processes respectively, $\theta_i = \hbar c / k\omega_i$ ($\hbar$—Planck constant, $c$—speed of light, $k$—Boltzman constant, $\omega_i$—phonon energy). 

In equation (3) we assumed that in both three- and four-phonon

### Table 1. Best fit parameters of curves modeled for FTIR spectra in figure 1.

| Sample | $\omega_{BN}$ (cm$^{-1}$) | $\gamma_{BN}$ (cm$^{-1}$) | $d_{BN}$ (nm) |
|--------|-----------------|-----------------|-------------|
| $S_1$  | 1367.69         | 22.60           | 8.47        |
| $S_2$  | 1367.15         | 20.25           | 15.66       |
| $S_3$  | 1368.66         | 22.40           | 60.28       |

![Figure 1. FTIR spectra measured at room temperature for three different samples ($S_1$, $S_2$, $S_3$) of epitaxial hBN layers on a Al_{2}O_{3} substrate (circles) with modeled curves (lines). The inset shows zoom of the hBN $E_{1u}$ vibrational mode peak.](image-url)
processes, there is the same energy decay product. This assumption is justified since in both decays the produced lower energy phonons are along the $M$–$K$ line in the dispersion relation, which is flat. The change related to the layer interaction with the substrate can be described with the following formula:

$$\Delta \omega(T) = \beta_{BN} \int_{T_c}^{T} \alpha_{sapphire}(T') - \alpha_{BN}(T') dT', \quad (4)$$

where $\alpha_{sapphire, BN}$ is the thermal expansion coefficient for sapphire and BN, $\beta_{BN}$ is the hBN Grüneisen parameter and $T_c$ is the temperature at which the layer on the substrate is relaxed. For the as-grown layer, it is the growth temperature, and for the delaminated layer it is room temperature. All the described contributions of $\omega_{BN}(T)$ dependency are plotted in figure 2(a).

We took the data for bulk hBN from the report of Segura et al [30] and fitted the curve using a model that does not include the layer-substrate interaction, which is reasonable for bulk material. This gives the following values of parameters: $\omega_0 = 1376$ cm$^{-1}$, $A = -7.25$ cm$^{-1}$, $B = -1.19$ cm$^{-1}$ and $\theta_1 = 369.78$ K. It corresponds to the decay to two phonons of energies 257 cm$^{-1}$ and 1119 cm$^{-1}$ in the three-phonon process, two phonons of energy 257 cm$^{-1}$ and one phonon of energy 862 cm$^{-1}$ in four-phonon process. These results are in good agreement with the literature values [26, 32].

In figure 2(b) we present the dependence of $\omega_{BN}(T)$ for the epitaxial layers. Both sets of results were collected for samples grown in the same MOVPE process. However, one of them was delaminated and transferred to a new sapphire substrate. The method used for delamination and transfer is as described in the literature [22]. The blue spheres related to the as-grown sample follow the same trend as the data for bulk material, which illustrates a blue dashed line. The line is drawn by adding a constant offset to the modeled curve for bulk hBN. The shift towards higher energies is due to a higher amount of defects in the epitaxial layer, which leads to additional strain. This additional effect does not allow for reliable parameters modeling because of an unknown temperature-dependent behavior of defects. It is suggested that the defect contribution should be linear [28]. Adding a further linear or quadratic term to the model would strongly influence other parameters which at this point are in good agreement with the literature values. We later show that defects indeed play an important role and that the assumption of a linear defect contribution is not always justified. For this reason, we provide only qualitative results.

The green spheres related to the delaminated sample exhibit a more significant decrease in phonon energy with increasing temperature. This decrease is most likely caused by a stronger layer-substrate interaction, as suggested by the yellow dashed line which was created by adding $\Delta \omega$ term to the blue dashed line. To cover the experimental data in a as wide as possible range, we assumed the hBN Grüneisen parameter $\beta_{BN} = -21$ cm$^{-1}$/%. This value is over two times lower than reported for hBN before [34]. The main reason for the change of layer-substrate interaction $\Delta \omega$ before and after delamination is the presence and lack of characteristic wrinkles (see supplementary materials). They are created during the cooling of the material after the growth process and can be removed in the delamination process [22]. The results presented in figure 2(b) imply that in the as-grown layer, the wrinkles can compensate for the layer-substrate strain. Consequently, the blue spheres run parallel to the modeled curve for the bulk material, as the blue dashed line suggests. The strain in the case of the as-grown epitaxial layer is eliminated by excess material stored in the wrinkles. The same behavior is observed for the delaminated layer below room temperature at which the delamination process occurred. When cooling the relaxed delaminated layer, the wrinkles can be created and compensate for the layer-substrate strain. Consequently, the $\omega_{BN}(T)$ trend below room temperature is similar for both delaminated and as-grown layers. Equally, the effect of the...
decrease in phonon energy related to $\Delta \omega_\alpha$ contribution for as-grown layers could be observed at much higher temperatures, which are closer to the growth temperature at which the wrinkles should disappear.

The discussed model explains the overall temperature dependence of $\omega_{\alpha}$. However, using this model, it is not possible to describe a giant, anomalous shift of the $E_{1u}$ phonon energy which we observed for some samples, which is the most striking result that emerges from our measurements. In figure 3 we present the $\omega_{\alpha}(T)$ dependence for a 20 nm thick layer grown in the two-stage epitaxy regime. One can notice an anomalous increase of phonon energy at 425 K for the 1st measurement. This increase cannot be explained by the presented model or the presence of the wrinkles since the anomaly can be observed for both as-grown (with wrinkle pattern) and delaminated layers (without wrinkle pattern) as presented in the supplementary materials. When performing consecutive temperature-dependent measurements, the anomaly softens and its maximum slightly moves towards lower temperatures as presented for 2nd and 3rd measurement. In the 4th temperature run, no anomalous phonon behavior is observed. As we have checked for other samples, the anomaly present in figure 3 is not an artifact of our data analysis method. Additionally, we independently performed a Lorentz curve fit. Even that basic data analysis gives the same result, which is the anomaly at the same temperature for the respective measurement run (see supplementary materials). Therefore, we observe a real physical phenomena.

We also observed the described anomalous behavior of $\omega_{\alpha}(T)$ dependence for other samples grown under different regimes under NH$_3$-rich conditions before and after the delamination process (see supplementary materials). The anomaly occurrence for different samples implies that the phonon upshift is not an accidental effect related to one specific sample, but can be reproduced when a special set of growth parameters is applied. The observation of the effect for both as-grown and delaminated layers implies that the effect cannot be attributed to the substrate, the thin AlN layer on Al$_2$O$_3$-hBN interface or the wrinkles, but is attributed to phenomena within the hBN layer.

In the following measurements presented in figure 3, there is an increasing difference in phonon energy between higher and lower temperatures. That means that the overall dependency exhibits an increasing slope in energy with increasing temperature. The same effect is observed when we compare the results for as-grown and delaminated layers in figure 2(b). In this case, it is most likely related to changes in the layer wrinkle pattern. As the result suggests, the wrinkle pattern can be changed for temperatures much lower than the growth temperature, as shown in the supplementary materials. The rearrangement of the wrinkles leads to an increase in the contribution of the layer-substrate interaction observed in the energy downshift for higher temperatures, as suggested by the brown curve in figure 2(a).

Once the anomaly vanishes after consecutive temperature runs, we can restore it by UV irradiation. This indicates an important role of defects in the hBN layer during the whole process. The presence of different kind of defects in this sample is evidenced by broad bands in the mid-bandgap photoluminescence spectrum (see supplementary materials). The anomaly measured after UV irradiation in the 5th run is much stronger and appears at higher temperature as presented in figure 3. The increase in phonon energy is $\sim$6 cm$^{-1}$. We propose the mechanism presented in figure 4 to explain the observed phenomenon. When the sample is exposed to UV light, electrons from the valence band are transferred to the conduction band (CB) (①). Then they can be trapped on a shallow defect $D_1$ just below the conduction band (②). Here, we assume that $D_1$ defect energy level is less than 1 eV below the conduction band, which has high degeneracy. The $D_1$ state can be filled during the growth process as well. These kinds of traps can store carriers for a significant time [35]. If the material has an additional defect state $D_2$ in between state

![Figure 3. $E_{1u}$ phonon energy as a function of temperature for the 20 nm thick sample grown in the Two-stage Epitaxy regime. Arrows indicate the anomalous behavior. The initial four temperature-dependent measurements lead to a softening of the anomalous phonon energy shift. After UV irradiation the anomalous effect is enhanced. Lines are guide to the eye only.](image-url)
D$_1$ and the CB, we can change the occupation probability of all three states during the measurement by changing the temperature (③). For a specific temperature, the occupation of the D$_2$ defect state reaches the maximum value. The change in electrical state of D$_2$ leads to a change of the distance of neighboring atoms, which is equivalent to the increase of configurational coordinate in the Frank–Condon energy diagram. Consequently, an inhomogeneous compressive strain is introduced. For such conditions, the phonon energy increases. This dependence between the electric state of the defect and the phonon energy suggests the presence of a strong electron-phonon coupling in those epitaxial hBN, in particular as the phonon energy suggests the presence of a strong electron-

 traps, and electrons occupy deeper donor levels. Further evidence for the presented mechanism is provided by the fact that the anomaly is observed in both directions, for an increase as well as for a consecutive decrease in temperature (see supplementary materials). We do not exclude that the presented mechanism could be occurring symmetrically for the valence band and acceptor states.

The microscopic nature of the defects in hBN is still unsatisfactorily known and understood. For this reason, it is hard to pinpoint defects D$_1$ and D$_2$. However, we have candidates that meet the described criteria. It has been reported that the energy levels of O$_N$ are shallow traps placed below the conduction band in hBN [36–40]. At very high temperature during the growth process, oxygen atoms diffuse and desorp from the Al$_2$O$_3$ substrate [41]. Consequently, the substrate can be a source of oxygen atoms in the hBN layer that replace nitrogen atoms. Such a defect has a low formation energy [36], so it should be present in all high-temperature grown epitaxial layers. The O$_N$ defect is therefore a good candidate for the D$_1$ defect.

The studied hBN layer was grown in the Two-stage Epitaxy regime in NH$_3$ rich conditions [20] which supports the creation of V$_B$ [36]. V$_B$ in 1- and 2- charge states increases the distortion between nitrogen atoms [36] which leads to lattice compressive strain in vicinity of the defect. Moreover, V$_B$ has an energy similar to that of the O$_N$ defect and the V$_B$–O$_N$ complex [36]. Therefore, we speculate that the D$_2$ defect can be a negatively charged boron vacancy. However, more research is needed to confirm our predictions.

The anomaly presented in figure 3 occurs in a narrower range of temperatures in comparison to the simulation in the inset in figure 4. That suggests that there are other effects that enhance the anomalous phonon energy behavior. Such an effect could be the piezoelectric response of boron nitride which is observed for different phases of sp$^2$-BN [42–44]. Such non-centrosymmetric phases, which exhibit piezoelectricity, are present in epitaxial boron nitride layers [21]. Moreover, there is evidence of a strong electrostrictive effect in boron nitride nanotubes [45, 46]. Electrostriction depends quadratically on the electric field. Therefore, the reverse of the field does not reverse the direction of strain. Consequently, the strain does not disappear when considering different randomly arranged BN grains. The deformation related to the electrostrictive effect is much greater compared to traditional piezoceramics [46]. Consequently, the electric field induced by charge redistribution on defect states would significantly influence the phonon energy change as observed in the experiment.

4. Conclusions

In this work, we studied the thermal response of the $E_{1u}$ phonon mode in boron nitride epitaxial layers using FTIR spectroscopy. The developed FTIR spectra analysis provided reliable information about the physical properties of epitaxial layers which are in good agreement with the XRR results. Both methods are complementary.
In our study, we investigated as-grown as well as delaminated layers. The results of temperature-dependent measurements emphasize the importance of layer wrinkles in the layer-substrate interaction. The wrinkles reduce the strain on the interface almost entirely. Consequently, the behavior of the epitaxial layer is similar to that of the bulk material.

Furthermore, we observed strong electron-phonon coupling, which can lead to a phonon energy increase up to 6 cm$^{-1}$. This anomalous behavior vanishes after sample heating and cooling cycles. Importantly, the process can be enhanced by UV irradiation. This effect can be explained by the presence of defects ($D_1$, $D_2$) close to the conduction band. The exact nature of such defects is still unknown. However, we speculate that these defects could be $O_N$ and $V_B$ or their complexes. By increasing the occupation of the upper $D_2$ energy state, we introduce an inhomogeneous compressive strain which leads to an anomalous increase in phonon energy. Most likely, the observed anomaly is enhanced by other effects such as piezoelectricity and electrostriction. However, more research is needed to investigate the exact properties of shallow impurity states and their influence on the properties of hBN.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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