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substrate deposition

structural asymmetry

hBN-C on Si(100) substrate

Heat flux [$10^{-7}$ W]

TR [%]

Substrate temperature [K]
Enhancement of thermal transport properties of asymmetric Graphene/hBN nanoribbon heterojunctions by substrate engineering

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Abstract

Two-dimensional heterostructures offer a new route to manipulate phonons at the nanoscale. By performing non-equilibrium molecular dynamics simulations we address the thermal transport properties of structurally asymmetric graphene/hBN nanoribbon heterojunctions deposited on several substrates: graphite, Si(100), SiC(0001), and SiO\textsubscript{2}. Our results show a reduction of the interface thermal resistance in coplanar G/hBN heterojunctions upon substrate deposition which is mainly related to the increment on the power spectrum overlap. This effect is more pronounced for deposition on Si(100) and SiO\textsubscript{2} substrates, independently of the planar stacking order of the materials. Moreover, it has been found that the thermal rectification factor increases as a function of the degree of structural asymmetry for hBN-G nanoribbons, reaching values up to \(\sim 24\%\), while it displays a minimum (\(\in [0.7, 2.4]\)) for G-hBN nanoribbons. More importantly, these properties can also be tuned by varying the substrate

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temperature, e.g., thermal rectification of symmetric hBN-G nanoribbon is enhanced from 8.8% to 79% by reducing the temperature of Si(100) substrate. Our investigation yields new insights into the physical mechanisms governing heat transport in G/hBN heterojunctions, and thus opens potential new routes to the design of phononic devices.

Keywords: G/hBN heterojunctions; thermal transport; molecular dynamics; substrate engineering.

1. Introduction

In recent years, heterostructures made of two-dimensional (2D) materials have drawn tremendous attention since they offer—through their different physical and chemical properties—additional tunability of the electrical and thermal response.[1, 2, 3, 4] Although most of these investigations have naturally focused on the study of electronic properties due to potential applications in next generation electronic devices, engineered heterostructures also offer a new avenue for engineering thermal transport properties.[5, 6, 7, 4, 8] Therefore, a deep understanding of the phononic properties of these materials will lead to the design of novel phononic devices such as thermal rectifiers, thermal transistors, and thermal logic gates,[9, 10, 11] similar to those proposed for carbon-based materials.[12, 13, 14] For instance, graphene/hexagonal boron-nitride (G/hBN) heterojunctions have been extensively studied due to the small lattice mismatch (2%) of the precursors,[15, 19, 20, 8, 21, 22, 23] and the synthesis of coplanar hybrid graphene and hBN monolayers has been successfully reported in several studies.[18, 20, 19] In particular, it has been shown that hBNC nanoribbons can be half-metallic or semiconducting depending on how graphene nanoribbons are embedded in the hBN matrix.[24] Interesting electrical rectifying effect and negative differential resistance have been theoretically predicted for graphene/hBN nanoribbon heterojunctions by using non-equilibrium Green’s functions in combination with density-functional theory (DFT).[25] An increasing interest in the thermal transport properties in such
heterojunctions is also taking place. Hong et al. have found, by using non-equilibration molecular dynamics (NEMD) simulations, that the interface thermal resistance decreases with increasing length of the graphene/hBN heterojunction and increases with increasing tensile strain independently of the heat flux direction. However, Chen et al. have recently demonstrated that heat current runs preferentially from the hBN to graphene domain, which enhances the thermal rectification in this heterostructure. Thermal conductivity in symmetric graphene/hBN heterojunctions has also been found, by using a normal mode decomposition approach, to depend on the periodicity and interface configuration of the superlattices. A minimum in the thermal conductivity at a critical pitch in Graphene/hBN superlattices was reported in Ref. By using Green’s function techniques, it has been shown that the bond type (C-N or C-B) along the interface sensitively controls the probability of scattering between the available phonon transport channels. Barrios-Vargas et al. showed by a finite-element based model that the thermal conductivity of polycrystalline structures of graphene and hBN is minimized for a hBN grain density of 70%, while this minimum was previously reported to occur at a density of 50% and 40% by using a real-space Kubo approach and equilibrium MD, respectively.

Nevertheless, all studies about thermal transport properties of Graphene/hBN heterojunctions have been carried out on free-standing structures, thus neglecting substrate effects. Recently, the impact of the substrate on the thermal conductance has been shown for graphene, silicon, molybdenum disulfide MoS$_2$, and phosphorene monolayers. Both experimental and theoretical investigations have shown that the substrate has always a negative effect on phonon transport in graphene, whereas the thermal conductivity of silicene can be either enhanced or suppressed by changing the surface crystal plane of a SiC substrate. On the contrary, by considering an amorphous SiO$_2$ substrate, the thermal conductivity of silicene displays a large reduction by almost 80% at 300 K. The interaction between MoS$_2$ mono-
layers and an amorphous SiO$_2$ substrate causes a lifting of the long-wavelength flexural modes leading to a reduction of the in-plane thermal conductivity.\cite{42} This strong dependence of the thermal transport properties on the substrate features highlights the importance of studying the effect of depositing coplanar graphene/hBN heterojunctions on specific substrates.

In this work, we investigate the influence of the substrate on the thermal transport properties of two types of heterojunctions, hBN-G and G-hBN nanoribbons, by means of non-equilibrium molecular dynamics (NEMD) simulations. We have considered four substrates: graphite, Si(100), 6H-SiC(0001), and alpha-quartz SiO$_2$(0001) with O-Si-O terminated surface. Our study is focused on coplanar symmetric and asymmetric graphene/hBN nanoribbon heterojunctions with zigzag interface (B-C bridge bonding), see Fig. 1(a). To quantify the degree of structural asymmetry of these nanostructures, the dimensionless quantity $W_{LR} = W_{\text{Left}}/W_{\text{Right}}$ has been introduced.\cite{44} Here, $W_{\text{Left}}$ and $W_{\text{Right}}$ are the widths of the left and right ends of the nanoribbon, respectively, and the case $W_{LR} = 1.0$ corresponds to a fully symmetric rectangular structure. The length ($L$) and width ($W$) of the nanoribbon change by the same scale, $W_{\text{Left}} = \sqrt{3}L/2$, when its size increases. We find out that the thermal transport properties of both heterojunctions are enhanced after substrate deposition and they can also be tuned by the substrate temperature $T_{\text{subst}}$ and the asymmetry degree $W_{LR}$.

In the next section, we describe the computational methodology and, then, proceed to discuss the results of the influence of these parameters on the thermal response of graphene/hBN nanostructures.

2. Computational methods

Non-equilibrium molecular dynamics (NEMD) simulations were carried out by using the LAMMPS code.\cite{45} Interactions among C, B, and N atoms were simulated by using an optimized Tersoff potential parametrized by Kinaci et al.,\cite{31} which has been successfully used to study thermal transport proper-
ties of many BNC nanomaterials. The atomic interactions in graphite, Si(100), SiC(0001), and SiO$_2$ substrates have also been modelled by a Tersoff potential. The coupling between the heterojunctions and substrates are described by a Lennard-Jones (LJ) potential, $V(r) = 4\chi \varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$, where $\varepsilon$ and $\sigma$ are the energy and distance parameters with units eV and Å, respectively; $\chi$ represents the coupling strength between the substrate material and the deposited heterojunction. To compare the results obtained for each substrate, we have used $\chi = 1$ for all the simulations. The parameters of the LJ potential for each element were taken from Refs. and are listed on Table S1 of the Supplementary Information. The distance between graphene/hBN heterojunctions and substrate was taken as $\sim 3.4$ Å (after geometry optimization). Simulations for free-standing materials have been done with free boundary conditions in all directions. We have also fixed the ends in X-direction (one layer) to avoid global rotations of the system during the simulation. For deposited materials, we have considered periodic boundary conditions on the XY plane and the substrate is large enough to avoid any interaction between the nanoribbon and its replica.

The standard velocity Verlet algorithm was used to integrate Newton’s equations of motion, and the MD time step was set to 0.1 fs. All investigated nanostructures have been initially relaxed using the quickstep method. Then, temperature equilibration runs for 5 ns at $T_0 = 300$ K were carried out by considering an NVT ensemble with a Nosé-Hoover thermostat (relaxation time equal to 0.1 ps). Once the temperature reached the required value, the thermostat was removed, and the NEMD simulations were carried out for 40 ns. The temperatures for left and right heat baths were defined as $T_L = (1 + \alpha)T_0$ and $T_R = (1 - \alpha)T_0$ for the forward direction of the heat flux (heat flows left-to-right or wider-to-narrower) and the opposite case for the backward direction (heat flows right-to-left or narrower-to-wider). We consider a temperature bias $\Gamma = |T_L - T_R| = 2\alpha T_0$ ($\alpha > 0$). Each heat bath extended over six atomic layers corresponding to a length of roughly $\sim 2.6$ nm. Time averages of the tempera-
ture and the heat current were carried out over the last 15 ns of the simulation. The temperature profile was then computed by dividing the system in a certain number of slabs and using the relation: 

\[ T_i = \frac{1}{3N_i k_B} \sum_{k=1}^{N_i} m_k v_k^2, \]

where \( N_i \) is the number of atoms in the \( i \)-th slab, and \( m_k \) and \( v_k \) correspond to the atomic mass and velocity of atom number \( k \), respectively. Furthermore, the calculated temperature for each slab, \( T_i \), was averaged over a pre-defined time interval to obtain a smooth temperature profile. To avoid spurious effects related to the specific choice of initial velocities, an average over five random choices of the initial velocity distribution was additionally performed.

To quantify the efficiency of thermal transport in both temperature bias directions, a thermal rectification (TR) ratio \( \eta \) is defined as:

\[ \eta[\%] = \left( \frac{|J_f - J_b|}{J_b} \right) \times 100, \]  

where the subscripts indicate whether the rectifier is operated at forward or backward direction of the heat flux. The heat currents \( J_{f,b} \) induced by the temperature bias \( \Gamma(T) \) are computed as \( J_{f,b} = \left( \frac{\partial E_{L,R}^{f,b}}{\partial t} + \frac{\partial E_{L,R}^{f,b}}{\partial t} \right)/2 \), where \( E_{L,R}^{f,b} \) are the total energies that have been added to or subtracted from the atoms in the left (L) and right (R) heat baths, respectively. It is worth noting that once the system reaches the steady state, the absolute values of the time derivatives have to be almost the same for left and right baths.

3. Results and discussion

Free-standing heterojunctions— We have first studied the thermal transport properties of both types of free-standing nanoribbon heterojunctions, hBN-G and G-hBN. For the sake of clarity, we focus on the T-shaped nanoribbon with \( L = 6.1 \) nm and \( W_{LR} = 3.0 \), since the results for the triangular shape are qualitatively similar (see the Supplementary Information). In Fig. 1(b) we show that independently of the system size and transport direction the heat flux decreases with increasing degree of asymmetry, as given by the parameter \( W_{LR} \).
This is a result of edge effects getting stronger once the number of atoms involved in the heat transfer is reduced.\textsuperscript{13, 44} The heat flux from hBN towards Graphene nanoribbons (forward direction) is always greater than the opposite direction for all hBN-G structures, in agreement with the results of Chen et al.\textsuperscript{29} For the fully symmetric case ($W_{LR} = 1.0$) it has been proven that this effect vanishes when periodic boundary conditions on the axis perpendicular to the transport direction are considered. That is, the heat flux is independent of the transport direction and $J_{hBN \rightarrow G} = J_{G \rightarrow hBN}$.\textsuperscript{28} In our case, the thermal rectification in hBN-G structures roughly displays a linear dependence on the asymmetry parameter $W_{LR}$, reaching values $\sim 21\%$ for $L = 6.1$ nm. On the contrary, for G-hBN nanoribbons a crossing point $W_C$ between the forward and backward heat fluxes at $W_{LR} \in [2.0, 3.0]$ is found. As a result, we have $J_{G \rightarrow hBN} > J_{hBN \rightarrow G}$ for $W_{LR} > W_C$, and therefore, the corresponding thermal rectification displays a non-monotonous dependence with respect to $W_{LR}$ with a minimum at the crossing point of the forward and backward heat fluxes, see Fig. 1(c). Notice that unlike single-material (hBN or Graphene) based nanoribbons, symmetric heterojunctions display rectification effects owing to interface effects which induce an asymmetric temperature profile and, hence, alter the heat flux intensity. A similar phenomenon was reported for heterojunctions made of carbon isotopes\textsuperscript{51} and graphene/silicene monolayers.\textsuperscript{52}

To gain insight into the influence of the degree of asymmetry on the thermal transport of the heterojunctions, we have performed a real-space mode analysis in the device region.\textsuperscript{44, 13} First, we computed the vibrational density of states as

\begin{equation}
S(\omega) = \sum_{jA} \sum_{\lambda} \sum_{\alpha} |\varepsilon_{jA,\alpha,\lambda}|^2 \delta(\omega - \omega_{\lambda}),
\end{equation}

where $\varepsilon_{jA,\alpha,\lambda}$ is the vibrational eigenvector component of mode $\lambda$ with polarization $\alpha = X, Y, Z$, and $\omega_{\lambda}$ is the frequency of the corresponding mode. The sum over $jA$ only includes atoms of a given type (A=C, N, and B). We notice that this quantity is calculated by first diagonalizing the dynamical matrix of
50 configurations taken every 20 ps during the last 1 ns of a given NEMD run, and then performing an average over five runs differing by the initial conditions (velocities), as previously mentioned.

In Fig. 2(a) and (b), we show $S(\omega)$ of T-shaped hBN-G and G-hBN nanoribbons with $L = 6.1$ nm and different $W_{LR}$. For both heterojunctions the vibrational density of states reduces with increasing $W_{LR}$. However, $S(\omega)$ of hBN-G nanoribbons is stronger modified in the frequency region $\omega \in [430, 1350]$ cm$^{-1}$, which is related to the fact that most of the vibrational modes involving carbon atoms are located within this spectral region. By contrast, in G-hBN nanoribbons, vibrational modes at lower ($\omega \in [0, 430]$ cm$^{-1}$) and higher ($\omega \in [1100, 1700]$ cm$^{-1}$) frequencies are suppressed due to the reduction in the number of B and N atoms with increasing $W_{LR}$. Additionally, in order to gain information on the degree of localization of the vibrational modes in different spectral ranges – which has been proven to be one of the mechanisms for thermal rectification – we have calculated the participation ratio $P_\lambda$ of each mode $\lambda$. It is defined as:

$$P_\lambda^{-1}(\omega) = N \sum_i \left( \sum_\alpha \varepsilon_{i\alpha,\lambda}^* \varepsilon_{i\alpha,\lambda} \right)^2,$$

with $\varepsilon_{i\alpha,\lambda}$ as the vibrational eigenvector component of atom $i$ and $N$ as the number of atoms in the system. $P_\lambda$ measures the fraction of atoms participating in a mode and hence varies between 1.0 for delocalized modes to $O(1/N)$ for localized modes. In Fig. 2(c) and (d), we can see that the localization behavior of the vibrational modes in asymmetric nanoribbons is complex and strongly depends on two factors: the planar stacking order and the frequency range. Low frequency modes (up to 350 cm$^{-1}$) in hBN-G nanoribbons are not much affected with increasing ribbon asymmetry, while the participation ratio is reduced for G-hBN nanoribbons. The influence of structural asymmetry is stronger in hBN-G nanoribbons in the range $\omega \in [350, 540]$ cm$^{-1}$, where the reduction in the number of C atoms localizes these vibrational modes. For G-hBN the mode delocalization can increase, $P \sim 0.45$ for $\omega \in [390, 560]$ cm$^{-1}$, by
making the nanoribbons more asymmetric. Higher frequency modes ($\omega > 1500 \text{ cm}^{-1}$) are strongly localized for both types of heterojunctions. Hence, in general heat transfer will be dominated by different spectral ranges depending on the junction type.

**Heterojunctions on substrates**— In a next step, we proceed to analyze the influence of substrate deposition on the thermal transport properties of the heterojunctions. For this, we have considered four substrates: graphite, Si(100), SiC(0001), and SiO$_2$. The setup for these calculations is shown in Fig. 3(a). Here, the heat baths are only located in the nanoribbons and the temperature bias is 60 K. The following results have been obtained by equilibrating the substrates at $T_{\text{substr}} = 300$ K which is the mean temperature in the nanoribbons. In Fig. 3(b), we show the temperature profile for forward and backward directions of free-standing and deposited hBN-G nanoribbons for $W_{LR} = 2.0$. It can be seen that the temperature profile is slightly affected by the substrate. The main changes are at the central region and at the heat bath-device interface. Also, the temperature drop at the interface for the heat flux in backward direction, $\Delta T_b$, is larger than the corresponding for forward direction, $\Delta T_f$. In fact, we have found that, independently of the substrate, $\Delta T_f$ and $\Delta T_b$ decrease and increase with increasing $W_{LR}$, respectively, i.e., heat flows preferentially in forward direction (direction of decreasing width). This takes place for both heterojunctions and it is correlated with the previous discussion of heat flux in free-standing nanoribbons. Similar observations were reported for pristine-hydrogenated carbon nanotube junction by increasing the H coverage.$^{53}$

To understand how substrate deposition affects the heat bath properties and, hence, the heat flux, we have calculated the corresponding vibrational density of states $\bar{S}(\omega)$ from the Fourier transform of the normalized autocorrelation function of atomic velocities in each polarization direction ($\alpha = x, y, z$):$^{54, 17}$

$$\bar{S}_\alpha(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^\infty e^{-i\omega t} \sum_{j=1}^N \frac{\langle v_{ja}(0)v_{ja}(t) \rangle}{\langle v_{ja}^2(0) \rangle} dt$$

(4)
where $\omega$ is the phonon frequency, and $v_{j\alpha}(t)$ denotes the velocity component of atom $j$ at time $t$. This density of states $\tilde{S}(\omega)$ is different to the one computed before, because here phonon scattering coming from the anharmonic terms included in the force fields is also considered, while $S(\omega)$ is computed within the harmonic approximation. In Fig. 3(c), we show $\tilde{S}(\omega)$ for the left (hBN) and right (G) heat baths in the forward direction of the heat flux for a free-standing hBN-G nanoribbon. Clearly, $\tilde{S}(\omega)$ values for G ribbons at 270 K are lesser than those one for hBN ribbons at 330 K in almost all the frequency range, but the overlap between both $\tilde{S}(\omega)$ is very large, which is favorable for heat transport. The main peaks of $\tilde{S}(\omega)$ are located at different frequencies for each substrate (see Fig. 3(d)). Graphite covers the same frequencies as the heterojunctions, whereas the power spectrum at 300 K for Si(100), SiC(0001), and SiO$_2$ substrates goes up to $\sim$800 cm$^{-1}$, $\sim$1100 cm$^{-1}$, and $\sim$1350 cm$^{-1}$, respectively. From Fig. 4 it can be seen that the substrates strongly alter vibrational modes at low frequencies, almost fully suppressing them until a certain material-dependent critical value $\omega = \omega_C$. This phenomenon is mainly caused by the coupling of the long-wavelength flexural modes with the substrate. The SiC(0001) substrate has the largest $\omega_C$ because it presents the strongest Van der Waals interaction with the heterojunction, which is measured by the $\varepsilon$ parameter in the Lennard-Jones potential (see Table S1). Accordingly, Graphite and SiO$_2$ substrates suppress less vibrational modes due to their smaller coupling parameter, as it is shown in the insets of Fig. 4. We have found that the mode suppression only affects the out-of-plane power spectrum ($\tilde{S}_z$) rather than in-plane one ($\tilde{S}_{xy}$). In fact, $\tilde{S}_z$ at low frequencies is reduced and its magnitude varies with the substrate (see insets in Fig. 4). This effect has also been theoretically reported in graphene and MoS$_2$ monolayers deposited on SiO$_2$ substrates.[42].

On account of these alterations in $\tilde{S}(\omega)$, it is expected that the overlap $\Lambda$ between the power spectrum of heat baths could change. Thus, we now analyze the overlap of $\tilde{S}(\omega)$ for the forward direction of the heat flux. To compute $\Lambda$, we have used the same expression as described in Ref. 51. Here,
we have found that independently of the planar stacking order of materials, the power spectrum overlap increases by effect of the substrate, i.e., the heat flux is enhanced. Another point to notice is that Λ for the heat flux flowing from \(hBN\rightarrow G\) is larger than that one for the flux from \(G\rightarrow hBN\) for symmetric free-standing and deposited nanoribbons,[29] which is in agreement with the previous heat flux values shown in Fig. 1(b). The maximum increment in \(hBN\)-\(G\) nanoribbons with \(W_{LR} = 1.0\) occurs when it is deposited on a \(Si(100)\) substrate and amounts to 5.7% of the corresponding value for the free-standing case (\(Λ^{hBN→G}(free) = 1.516\)). Despite showing the strongest suppression of out-of-plane modes at low frequencies, the overlap slightly increases for deposition on \(SiC(0001)\) substrate (3.8%). For a \(G\)-\(hBN\) nanoribbon deposited on \(Si(100)\), the overlap is also maximal and equal to \(Λ^{G→hBN}(Si(100)) = 1.584\), which corresponds to an increment of 6.4% of \(Λ^{G→hBN}(free)\). The \(SiO_2\) substrate improves the power spectrum overlap for both nanoribbons: \(Λ^{hBN→G}(SiO_2) = 1.589\) and \(Λ^{G→hBN}(SiO_2) = 1.570\). Additionally, the overlap of \(\bar{S}_{xy}(\omega)\) does not change at all after depositing the nanoribbons on substrates (< 4% of \(Λ^{(free)}_{xy}\), \(hBN\)-\(C=1.714\) and \(C\)-\(hBN=1.701\)). Nevertheless, for \(\bar{S}_{z}(\omega)\), the overlap increases up to \(\sim 11%\) of \(Λ^{(free)}_{z}\) for \(hBN\)-\(G\) (1.889) and \(G\)-\(hBN\) (1.685) nanoribbons, becoming larger than the corresponding values to in-plane contributions. As a result, out-of-plane modes will have an important contribution for the thermal transport properties in these nanomaterials, as it has been previously reported for other 2D nanostructures.[6] [42] [26] [52] A similar phenomenon happens for the heat flux in the backward direction and varying asymmetry degrees. It is worth mentioning that the magnitude of the variations in spectral overlap can be controlled by the temperature bias \(Γ(T)\) between the heat baths. Hence, the increment of power spectrum overlap in the heterojunctions will enhance their heat flux and alter the behavior of the thermal rectification.

In order to better capture the influence of the substrate on heat transport, we have computed the interface thermal conductance (ITR, or Kapitza resistance),[53]
which is defined as $K_{f,b} = \frac{A\Delta T_{f,b}}{J_{f,b}}$, with $\Delta T$ as the temperature drop at the material interface and $J$ the heat flux. $A = W_A h$ is the transversal area of the nanoribbon, $W_A = (W_L + W_R)/2.0$ (effective width) and $h = 0.33 \text{ nm}$ (height of the ribbon). For hBN-G nanoribbons, ITR for backward direction of the heat flux is always greater than the forward direction (see Fig. 5(a)). This only happens for G-hBN nanoribbons with $W_{LR} \geq 2.0$ (see Fig. 5(b)). The large difference between $K_f$ and $K_b$ for $W_{LR} \geq 3.0$ is mainly due to the large $\Delta T_b$ produced by the strong structural asymmetry of nanoribbons, e.g., for a hBN-G nanoribbon with $W_{LR} = 5.0$ deposited on Si(100) substrate: $\Delta T_f \sim 8 \text{ K}$ and $\Delta T_b \sim 32 \text{ K}$. The same effect has been found for all the studied substrates. Moreover, the interface thermal resistance, independently of the flux direction, is reduced after deposition, i.e., the thermal conductivity is enhanced in presence of a substrate, which confirms the preceding analysis. Interestingly, our results are in contrast to those found in supported graphene, where the substrate produces a negative effect in its thermal conductivity. For hBN-G heterojunctions, by considering a Si(100) substrate, $K_{f,b}$ shows the strongest reduction after increasing the asymmetry degree. On the other hand, Graphite and SiO$_2$ substrates lead to the largest increase of the thermal conduction in asymmetric G-hBN nanoribbons. Note that ITR for G-hBN heterojunction also displays the same crossing point found in the analysis of the $J(W_{LR})$-curve for forward and backward directions (see Fig. 1(b)).

Next, we have plotted the variation of the ratios $K_b/K_f$ and $J_f/J_b$ at each $W_{LR}$ value for both heterojunctions deposited on all the substrates (see Fig. 5(c) and (d)). The behavior of $J_f/J_b$ for free-standing and deposited nanoribbons is very similar. In fact, the thermal rectification (related to $J_f/J_b$, see Eq. 4) for deposited hBN-G nanoribbons with $W_{LR} \leq 5.0$ is smaller than the corresponding values for free-standing ribbons. At $W_{LR} = 7.5$, all the substrates, with the exception of Si(100), improve the thermal rectification of the heterojunction, which can reach values up to $\sim 24\%$, comparable to other asymmetric
structures, and heterojunctions. The scenario is quite different for deposited G-hBN nanoribbons. Their $\eta(W_{LR})$-curve also presents a minimum at $W_{LR} = 2.0$ as in the free-standing case, but its value has been increased for ribbons with $W_{LR} \geq 3.0$ up to $\sim 20\%$. The rectification effect in G-hBN nanoribbons with $W_{LR} = 2.0$ can be strongly suppressed by depositing it on a graphite substrate, $\eta \sim 0.7\%$. These trends are verified by computing the interface thermal rectification defined using $K_b/K_f$ instead of $J_f/J_b$, as it has been done in other related works. Clearly, $K_b/K_f$ only increases because of the considerable magnitude of $K_b$. We remark that a non-linear behavior for $K_b/K_f$ vs $J_f/J_b$ was obtained for asymmetric nanoribbons, which is different to the linear behavior expected by varying the temperature bias between the heat baths.

Influence of the substrate temperature $T_{subst}$ — For the sake of simplicity we have addressed this issue only in the case of a structurally symmetric hBN-G nanoribbon ($W_{LR} = 1.0$). We found that, independently of the type of substrate, the heat flux for forward direction slightly decreases by increasing $T_{subst}$, while by reversing the temperature bias a considerable increment of the heat flux is obtained. In Fig. 6(a), we show the results for graphite and Si(100) substrates which correspond to the weakest and strongest influence on the heat flux as a function of $T_{subst}$, respectively. This phenomenon yields an intersection between $J_f$- and $J_b$-curves at $T_{subst} \sim 380$ K for graphite and $T_{subst} \sim 313$ K for Si(100), which produces a full suppression of the rectification effect, i.e., $\eta = 0$. This occurs due to the fact that $\bar{S}(\omega)$ at low frequencies increases by heating up the substrate (see Fig. S2 in the Supplementary Information). Thus, the power spectrum overlap of the heat baths is modified and, consequently, the heat flux.

It has also been found that the high density peaks at low frequencies in the power spectrum of Si(100) (see Fig. 3(c)) make nanoribbons (deposited on this substrate) to have the largest increment of $\bar{S}(\omega)$, followed by SiO$_2$ and SiC(0001) (see Fig. S3 in the SI). As seen in Fig. 5(b), the thermal rectification can reach values up to $\sim 79\%$ when the Si(100) substrate is equilibrated at 100 K, whose
magnitude is of the same order as values reported for more complex structures such as graphene Y-junctions \cite{56} and graphene/CNT heterostructures. \cite{57, 8}

Whereas nanoribbons deposited on graphite substrates display the lowest thermal rectification for almost the entire temperature range $[100,500]$ K. Around $T_{\text{sub}} = 300$ K, which is the mean temperature of the nanoribbon (NEMD run), the influence of the type of substrate varies. Results for SiC(0001) and SiO$_2$ substrates are shown in the Supplementary Information. In short, the thermal transport properties of the heterojunctions can be sensitively controlled by tuning the substrate temperature without the need of modifying the geometry of the heterojunctions.

4. Conclusions

To conclude, we have performed a NEMD study of the influence of substrate deposition and degree of structural asymmetry on the thermal transport properties of coplanar G/hBN nanoribbon heterojunctions with zigzag interface. We considered four substrates: graphite, Si(100), SiC(0001), and SiO$_2$. It has been found that the interface thermal resistance is reduced upon substrate deposition. This is mainly due to the suppression of out-of-plane modes at low frequencies that produces an increment of the spectral overlap between the power spectrum of the heat baths before and after reversing the temperature bias. Moreover, we have obtained that the thermal rectification effect is reduced for small $W_{LR}$ when hBN-G nanoribbons are deposited on a given substrate, but increases with increasing asymmetry, reaching values as large as $\sim 24\%$ for $W_{LR} = 7.5$. Deposited G-hBN nanoribbons also display a minimum in the thermal rectification as for the free-standing case, but for $W_{LR} \geq 3.0$ it becomes larger than in the free-standing situation. We have also shown that the substrate temperature plays an important role in determining the magnitude of the thermal response in these nanomaterials, making possible to reach thermal rectification values of $> 50\%$ without altering their geometry. Our results thus provide a deeper insight into the role of substrates in influencing the thermal response of pla-
nar heterostructures and thus open the possibility of substrate engineering for controlling thermal transport in two-dimensional heterostructures.

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Figure 1: (a) Schematic representation of free-standing hBN-G heterojunctions with zigzag interface (B-C bridge bonding). The degree of asymmetry is measured by $W_{LR} = W_{Left}/W_{Right}$. (b) Variation of heat flux after increasing the asymmetry degree for hBN-G and G-hBN nanoribbons. We compare the results for two different system size ($L = 6.1$ nm and 9.2 nm). (c) Thermal rectification as a function of $W_{LR}$ for both type of nanoribbons. We also shown the $\eta$ values for pure graphene and hBN nanoribbons.
Figure 2: Real-space mode analysis of asymmetric free-standing heterojunctions. Vibrational density of states and participation ratio at different asymmetry degree $W_{LR}$ for (a,c) hBN-G and (b,d) G-hBN nanoribbons, respectively. The results are for the forward direction of the heat flux. We also highlight the frequencies corresponding to the vibrational modes of BN atom pairs (solid bar line) and C atoms (dashed bar line).
Figure 3: (a) Scheme of the setup used to perform NEMD simulations of deposited hetero-junctions. (b) Temperature profiles for forward (○) and backward (□) direction of the heat flux for a hBN-G nanoribbon with $W_{LR} = 2.0$ deposited on Si(100) and SiC substrates. We also show the profiles for the free-standing case. Vibrational density of states, computed by using Eq. 4, of (c) the heat baths in a hBN-G nanoribbon with $W_{LR} = 1.0$ for a heat flux in forward direction and (d) the studied substrates at 300 K.
Figure 4: Total vibrational density of states of the heat baths in symmetric (a,c) hBN-G and (b,d) G-hBN nanoribbon heterojunctions ($W_{LR} = 1.0$) deposited on a given substrate ($T_{\text{substr}} = 300 \text{ K}$). The results are for the forward direction of the heat flux. Inset: the out-of-plane mode contribution, $S_z$. For comparison, we also show the results for the free-standing case (solid lines with circles). $\omega_C$ represents the lift in frequency after substrate deposition.
Figure 5: Interface thermal resistance of deposited (a) hBN-G and (b) G-hBN nanoribbon heterojunctions as a function of $W_{LR}$ for the hat flux at forward ($K_f$) and backward ($K_b$) direction. Ratios of ITR $K_b/K_f$ vs ratios of heat flux $J_f/J_b$ for deposited (c) hBN-G and (d) G-hBN nanoribbon heterojunctions. The results for the free-standing case are also shown (filled circles).

Figure 6: (a) Variation of the heat flux in the forward (>) and backward (<) directions for symmetric hBN-G nanoribbons deposited on graphite and Si(100) substrates as a function of the substrate temperature, $T_{substr}$. The arrows indicate the situation $J_f = J_b$ for each substrate. (b) Substrate temperature dependence of thermal rectification for hBN-G nanoribbons.