A Molecular Dynamics Study of Thermal conductivity in Monolayer GaN Nanoribbon

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***Abstract*—Nowadays 2D materials like Graphene, Silicene, Stanene and single layer transition metal dichalcogenides (e.g., MoS2, WSe2,MoTe2,), are drawing significant attention in the research arena due to their superior electrical, thermal and opto-electronic properties to their bulk counterparts. In this study, we have investigated the thermal transport properties of single layer zigzag gallium nitride (GaN) nanoribbon using equilibrium molecular dynamics simulations. The calculated room temperature thermal conductivity of 20 nm $\times$ 2 nm single layer GaN nanoribbon using tersoff inter-atomic potential is 2.04 W/m-K. The temperature and sample size dependence of thermal conductivity have also been studied. For a particular sample size, the thermal conductivity of GaN nanoribbon decreases with increasing temperatures. On the other hand, an opposite pattern is observed for length variation i.e. thermal conductivity increases with the increase in ribbon length keeping the temperature constant. Our study further includes the investigation of the thermal transport of defected GaN nanoribbon. The thermal conductivity of defected GaN sample has been estimated by incorporating defects of different concentration [1% to 5%] for different operating temperatures [100K to 500K]. Our study shows that the thermal conductivity reduces drastically with the increase of defect concentration. We have also calculated phonon density of states (PDOS) for pristine and defected GaN nanoribbon to provide better understanding of these phenomena. Our study would be helpful for further investigation of thermal transport in single layer GaN based devices.**

***Index Terms*—Equilibrium Molecular Dynamics (EMD), Green-Kubo method, GaN nanoribbon, Tersoff inter-atomic potential, Thermal conductivity.**

I. Introduction

Grapehene is considered as the representative of two dimensional (2D) materials with excellent electrical, thermal and mechanical properties [1]–[6] and being inspired with these outstanding characteristics, the researchers are now focusing on many other single layer to few layers materials. Experiments are being carried out on other two dimensional materials like silicene, germanene and single-layer molybdenum disulfide (SLMoS2) due to their unique properties [7], [8]. Single-layer gallium nitride (GaN), a direct bandgap 2D material with high quantum efficiency which belongs to the III-V group, is suitable for optoelectronic, high-power and high-frequency device applications because it has wide band gap of 3.4 eV at room temperature [9]. Due to its lower thermal conductivity mono layer (ML) GaN is a particularly beneficial candidate for thermoelectric devices. Although the research schemes of 3D to 1D GaN materials are gradually maturing, research on ML GaN is yet to explore. The application of ML GaN nanosheets in light-emitting diodes has been predicted by Yeh *et al.* [10]. Moreover, the recent synthesis of monolayer GaN further draws attention of researchers towards this promising 2D material [11]. Due to its low dimensionality, the physical and chemical properties of ML GaN would have diversity, which can further affect the applications of relevant electronic devices. The possible device applications of ML GaN is inevitably related to its thermal transport properties and thus calls for an elaborate investigation of the thermal conductivity (κ) of this emerging material including the dependence of various parameters on thermal conductivity.

Qin *et al.* have solved Boltzmann transport equation (BTE) based on first-principles to study the phonon transport properties of planar structure of ML GaN and calculated its thermal conductivity at room temperature to be 14.93 W/m-K [12]. Zou *et al.* reported the κ of free standing GaN nanowire with diameters in the range of 20 nm to 140 nm solving BTE. In this paper, we have carried out equilibrium molecular dynamics (EMD) simulation to calculate the κ of 20 nm$\times$2 nm GaN nanoribbon structure varying the temperature from 100K to 500K using an tersoff inter-atomic potential. To study the impact of different parameters of the sample structure and temperature on thermal transport of ML GaN, κ of ML GaN nanoribbon has been reported by varying the length ranging from 10 nm to 50 nm keeping the width constant at 2 nm and temperature from 100K to 500K. To have better insight on thermal transport of defected GaN nanoribbon, defects of different concentration have been incorporated in the sample ranging from 1% to 5%. The phonon density of states (PDOS) has also been calculated to support the obtained results.

II. Methodology

Molecular dynamics is a simulation method that allows the time evolution of a system of interacting particles using Newton's equations of motion which states that,

$$m\frac{d^2r_i}{dx^2} = -\frac{\partial V}{\partial r_i} \tag{1}$$

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here, m represents the mass of the particle, r_i represents the position of the particle i and V is the inter-atomic force as a function of particle's position. Verlet algorithm [13] is used as the integration scheme that estimates the position and velocity of the particle i at a given time interval. The time step used in the integration scheme is given by eqn.2,

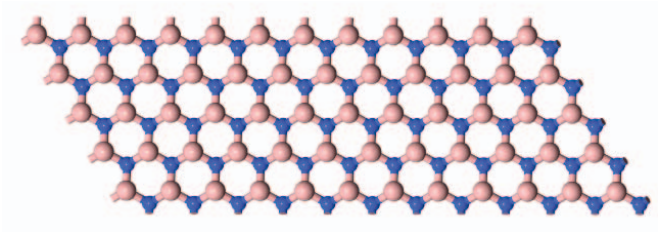
$$\tau = \sqrt{\frac{m\sigma^2}{K_B T}} \approx 1ps \tag{2}$$

here, m represents the mass of the particles and the value of σ approximately equals to a conventional atomic diameter. The estimation of thermal conductivity using Green-Kubo method which is based on EMD simulation is derived from the fluctuation-dissipation and linear response theorem [14]. The thermal conductivity in a particular direction (Kx) which is related to heat current auto correlation function (HCACF) is calculated using eqn.3

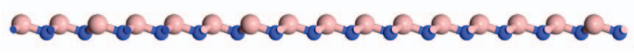
$$Kx = \frac{1}{VK_B T^2} \int_0^\tau < j_x(t).j_x(0)dt > \tag{3}$$

here, V represents the volume of the sample, K_B is the Boltzmann constant, T and τ denote the temperature and correlation time respectively. The correlation time is defined as the required time for significant decay of HCACF.

In our present study, we have performed our simulation using LAMMPS and in order to incorporate the bonding interactions between Ga and N in GaN nanoribbons, we have utilized the tersoff inter-atomic potential with parameters suggested by Albe *et al.* [15]–[17]. For calculating the PDOS of GaN nanoribbons for various defect percentage, *fix Phonon* package of LAMMPS has been engaged to estimate the dynamical matrices. And then, an auxiliary post-processing code phana is used to calculate PDOS from the obtained dynamical matrices.



(a)



(b)

Fig. 1: Atomic structure of zigzag GaN nanoribbon. (a) Top view and (b) Front view . [Here the purple and blue spheres represent Ga and N atoms respectively]

In our present study, the thickness of GaN nanoribbons is set to 3.74 Å [12] and periodic boundary condition (PBC) was applied along the zigzag direction. At first , the system with fixed number of atoms runs under constant volume and constant temperature (NVT) ensemble, followed by constant volume and constant energy (NVE) ensemble for energy minimization. Then the system remains in production run until a reasonable decay of HCACF and converged κ is reported. Fig.1 illustrates the structure of buckled zigzag GaN nanoribbons used in our present study. To incorporate defects in the sample, we have considered arbitrary removal of Ga and N atoms from the sample shown in Fig.2.

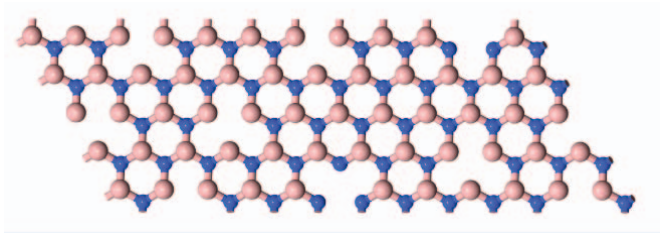


Fig. 2: GaN nanoribbon with defects. [Here the purple and blue sphere represents Ga and N atoms respectively]

III. Simulation Result and Discussion

The average κ of 20 nm×2 nm GaN nanoribbon at room temperature using tersoff inter-atomic potential found in our study is 2.04 W/m-K. Our estimated κ is significantly lower than other 2D materials like Graphene nanoribbon (GNR) [∼3000 W/m-K] [18], MoS_2 [34.5 W/m-K] [19], and hexagonal boron nitride, h-BNNR [554 W/m-K] [20]. Moreover, the single layer GaN sample shows a significant deviation in thermal conductivity than its respective bulk counterpart. Jeżowski *et al.* found ∼220 W/m-K as the κ of 3×0.05×5 mm^3 GaN structure [21]. The κ of ML GaN nanoribbon is less than its bulk structure due to having less number of phonon branches in GaN nanoribbon, lower group velocity and phonon lifetime than its corresponding bulk structure [22].

The κ of freestanding GaN nanowire with diameter 20 nm is reported as 6.49 W/m-k by solving BTE [23]. The relatively lower value of thermal conductivity found in our study is mainly attributed to the buckled structure of GaN nanoribbon considered in our simulation. In a buckled structure more scattering channels are provided by ZA mode which result in a lower value of κ [24].

Fig.3 shows the change in κ with the variation of sample size (length).The figure reveals that κ increases as length increases and this result is coherent with the recent study of Qin *et al.* [12]. This behavior of ML GaN is analogous to single layer suspended Graphene in which κ increases with the increase of sample length [25]. Moreover, it can be observed from the Fig.3 that as the length increases, thermal conductivity becomes less sensitive to the variation of length. This is due the fact that when length increases the mean free path (MFP) reduces as phonon-boundary scattering becomes less dominant.

The dependence of temperature on κ of a 20 nm × 2 nm GaN nanoribbon is shown in Fig.4. As anticipated, the figure

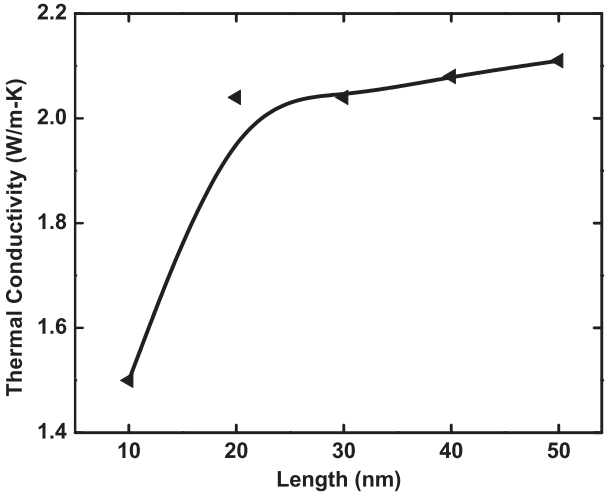


Fig. 3: Room temperature thermal conductivity of mono layer GaN nanoribbon as a function of length keeping the width constant at 2nm.

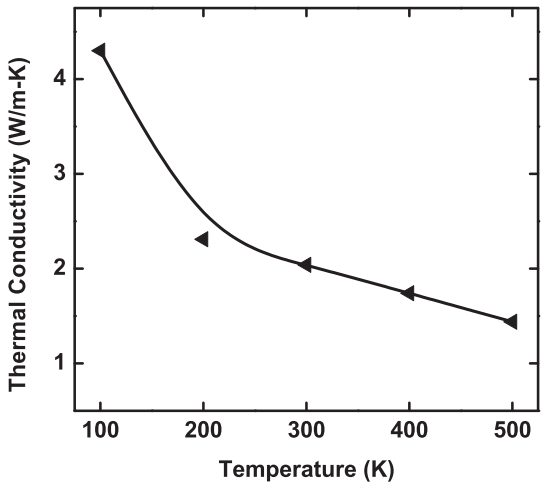


Fig. 4: Average thermal conductivity as a function of temperature for a 20 nm x 2 nm mono layer GaN nanoribbon

shows a decreasing trend at higher temperature. When temperature is high, phonon-phonon Umklapp scattering becomes dominant as the amount of high frequency phonon increases causing a decrease in κ.

During the fabrication process, some unintentional defects might be introduced within the sample. Therefore, considering the inaccuracy of fabrication technology, we have incorporated defects i.e. vacancy by removing Ga and N atoms arbitrarily and considered defects concentration ranging from 1% to 5%. We have engaged EMD simulation to analyze the impact of defects on the κ of GaN nanoribbon of size 20 nm x 2 nm at different temperatures as shown in Fig.5. The figure shows that the κ of pristine monolayer GaN nanoribbon at room temperature is $\sim$2.04 W/m-K while it drops to $\sim$1 W/m-K for defected ML GaN nanoribbon at 5% defect percentage. Moreover, the κ shows a decreasing trend at elevated temperature for different defect concentrations considered in this study.

Fig.6 shows the percentage decrease in κ of 20 nm $\times$ 2 nm defected GaN nanoribbon in comparison with its pristine counterpart for different temperatures. As elucidated in Fig.6, the reduction in thermal conductivity becomes less sensitive to defects as the percentage of defects incorporated in the sample increases. Moreover, as the temperature increases the percentage decrease of thermal conductivity at a particular defect concentration degrades slightly. This is due to the fact that nanostructuring MFP of phonons is governed by the grain boundaries and it is not dependent on the phonon frequency and the temperature to some extent. In our study, percentage decrease of κ due to defects is calculated using the following formula :

$$\frac{\kappa_{pristine} - \kappa_{defected}}{\kappa_{pristine}} \times 100 \quad (4)$$

The reduction of κ of defected GaN nanoribbon is mainly due

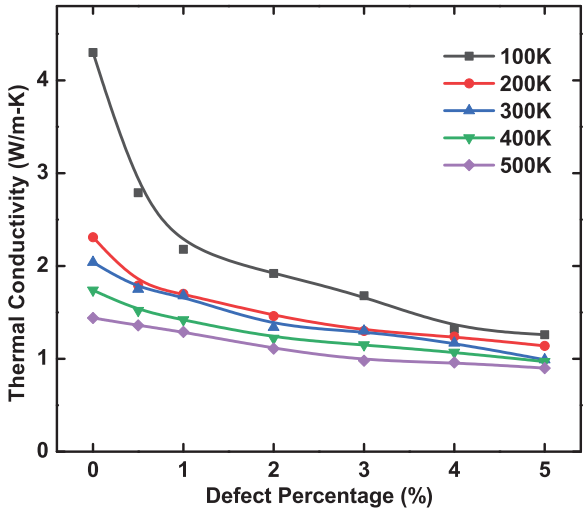


Fig. 5: Average thermal conductivity of GaN nanoribbon as a function of defect percentage for different temperatures.

to the localization of phonons around the vacancies.

To further anticipate the reduction of κ due to defects in GaN nanoribbons , we have reported PDOS for both the pristine and defected GaN at 2% vacancy concentration at room temperature as shown in Fig.7. The large difference in atomic radius between Ga and N, unlike the honeycomb structure of graphene which consists of only C atoms, affects the phonon transport properties significantly. Our result also exhibits that there is a large bandgap between low and high frequency branches primarily caused by the different atomic masses of Ga ($\sim$69.7) and N ($\sim$14). These results are coherent with the result found by Qin *et al.* [12]. The vibration of

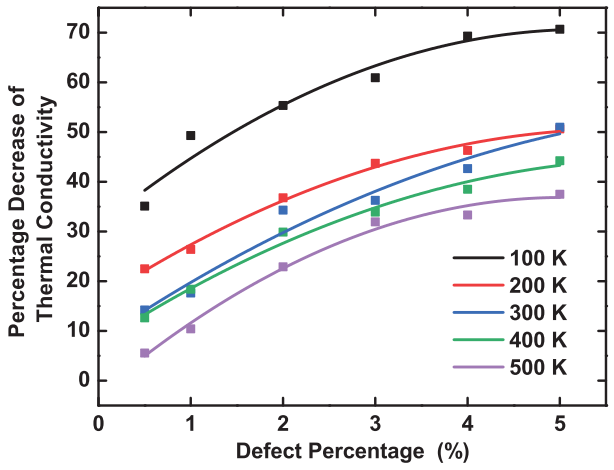


Fig. 6: Percentage decrease of thermal conductivity of mono layer GaN nanoribbons for different temperatures as a function of defect percentage.

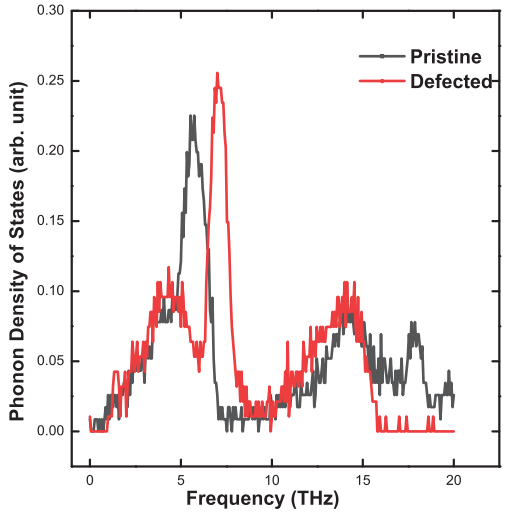


Fig. 7: Phonon density of states (PDOS) for mono layer pristine and defected GaN nanoribbon. Here the black and red curve represent PDOS for pristine and defected GaN nanoribbon respectively.

the light N atom mainly contributes to the high-frequency optical phonon branches above the gap which could reach up to 20 THz at the Γ point [12]. The high density of low frequency phonon for defected ML GaN nanoribbon results in a higher rate of anharmonic Umklapp scattering and decreased thermal conductivity. Additionally, the higher magnitude of the peak PDOS for defected GaN is responsible for flatter phonon dispersion curve [26] which further indicates the lower phonon group velocity and hence the reduction of κ in the defected GaN nanoribbon. Therefore, defects can be intentionally introduced into the sample to tune the κ of GaN nanoribbon.

IV. Conclusion

In summary, we have explored thermal transport in monolayer GaN nanoribbons using Equilibrium Molecular Dynamics simulation. We have reported the variation of thermal conductivity with the sample length and operating temperatures. The estimated average thermal conductivity of 20 nm $\times$ 2 nm GaN nanoribbon at room temperature is 2.04 W/m-K and the thermal conductivity shows an increasing trend with the increase of the sample length. On the other hand, the average thermal conductivity of GaN nanoribbons decreases with the increase in temperature. To validate the application of GaN nanoribbons in higher temperature region and considering the defects incorporated during the synthesis process of 2D materials, we have observed thermal conductivity by incorporating defects in the ribbons for different temperatures. The effects of increased operating temperatures and vacancy defects cause the drastic reduction of thermal conductivity which actually validates the application of GaN nanoribbons as a good thermoelectric material. To further investigate the phonon thermal transport in GaN nanoribbons, we have calculated the phonon density of states of pristine and defected GaN nanoribbons in support of the obtained results.

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