

Phonon thermal transport in alloyed and hybrid zigzag nanoribbons of gold and silver

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We have investigated phonon transport in alloyed ($\text{Au}_{0.5}\text{Ag}_{0.5}$) and hybrid (Au_mAg_n ; here m and n are indices for the width of respective nanoribbons) zigzag nanoribbons of gold and silver. To this endeavour, we have employed the non-equilibrium Green's function approach integrated with force-field methods as implemented in the General Utility Lattice Program. The phonon thermal conductance k_{ph} has been computed and its dependence on width of nanoribbons and temperature has been explored. It has been found that k_{ph} increases linearly with the width for the alloyed nanoribbons. However, the hybrid nanoribbons exhibit the linear behavior only for the special case of $m=n$. The calculated results of k_{ph} are compared with the corresponding pristine nanoribbons. Interestingly, we find that both alloying and hybridization result in a significant reduction in k_{ph} . For a comparable width, the reduction is more in the alloyed nanoribbons. Thus, our study suggests that alloying may be exploited to suppress the phononic thermal conductance, and hence to enhance the thermoelectric efficiency of nanoribbons.

Keywords: Hybrid nanoribbons, Phonon transport

1 Introduction

In past few decades, the synthesis of metal nanostructures with specific size and morphology has been the focus of research due to their potential applications in electronic, optical, optoelectronic, sensing, biomedical, etc. devices^{1,2}. It is now well established that the intrinsic properties of metal nanostructures can be fine-tuned by controlling their shape, size, dimensionality, and structure^{3,4}. One-dimensional nanostructures such as nanowires, nanotubes, and nanoribbons have gained much attention due to their promising applications as circuitry elements in nano-electronics^{5,6}. Particularly, nanoribbons (NRs) have been extensively studied because they constitute an excellent system for probing the dimensionally-confined transport phenomena^{7,8}. Synthesis of silver NRs by heating an aqueous dispersion of spherical colloids of silver with a diameter of 3.5 nm has been reported⁹. In literature, there have appeared some important studies exploring the thermoelectric potential of these nanostructures¹⁰⁻¹², with main thrust on achieving as higher thermoelectric efficiency as possible. Recently, Kapoor *et al.*¹³ have made a systematic analysis of the structural and electronic properties of Au and Ag NRs

modeled in zigzag (ZZ) and armchair (AC) geometries using the density functional theory (DFT). Singh *et al.*¹⁴ have calculated the phononic contribution to thermal conductance in these NRs using the non-equilibrium Green's function (NEGF) approach. It has been predicted that the phononic thermal conductance k_{ph} increases linearly with the width of NRs. More recently, Singh *et al.*^{15,16} have presented a comprehensive study on thermoelectric transport properties of pristine and alloyed noble metal atomic wires modeled in different topologies using the NEGF approach. Importantly, it has been shown that the thermoelectric efficiency of atomic wires can be enhanced significantly via topology and alloying. Motivated by this, we undertake in this work a theoretical study on the effect of alloying and hybridization on the phonon thermal transport in ZZ-edge type NRs of Au and Ag. We use the (semi-classical) General Utility Lattice Program (GULP)¹⁷ code together with the NEGF approach.

2 Nanoribbons Model and Computational Details

We consider alloyed and hybrid NRs of Au and Ag in ZZ configuration as shown in Fig. 1. Each NR is placed in the y - z plane with its length taken along the transport direction (i.e., z -axis). Here, m and n represent indices for the width of NRs. The real width

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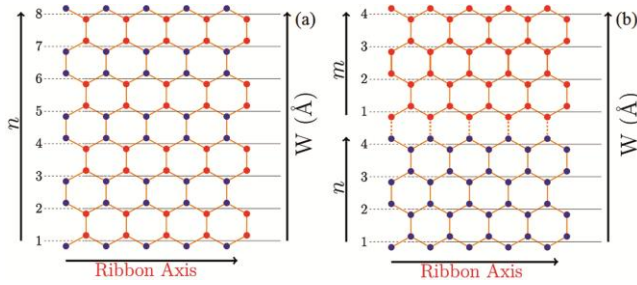


Fig. 1 – A ball-stick representation of (a) alloyed (b) heterostructured zigzag nanoribbons n and m represent the index number for the width of the NR. W is the optimized width of the NR.

W of NRs is the maximal distance between outermost atoms in the y direction. To calculate dynamical properties of NRs, we have made use of the GULP code¹⁷. The inter-atomic potential is obtained by the embedded atom method (EAM). The detailed parameterization of the potential has been presented by Sheng *et al.*¹⁸. The relaxation of structure is carried out by using the LBFGS algorithm until force on each atom is less than 0.001 eV/\AA . A vacuum gap of more than 25\AA is chosen in the x and y directions to prevent interactions between neighboring NRs. For each structurally optimized nanoribbon, the dynamical matrix K is calculated.

Here, the force constant is determined from the second derivative of potential energy with respect to atomic positions in Cartesian space and thus, we include only the harmonic interactions. The phonon transmission function $\tau_{ph}(E)$ is then calculated using the NEGF approach¹⁹⁻²². Here, the K matrix is passed to the PHtrans, a post-processing utility of SIESTA^{23,24}, by using the Python based utility SISL^{25,26}. Finally, the phononic thermal conductance k_{ph} is evaluated using the Landauer formula for the phonon heat current as:

$$\kappa_{ph} = \frac{1}{h} \int_0^{\infty} \tau_{ph}(E) E \left(\frac{\partial f_B(E, T)}{\partial T} \right) dE \dots (1)$$

where $f_B(E, T) = \{\exp(E/k_B T) - 1\}^{-1}$, is the distribution of phonons in each electrode.

3 Results and Discussion

First of all we calculate the phonon transmission function $\tau_{ph}(E)$, the main ingredient involved in the calculation of k_{ph} . Numerical results of $\tau_{ph}(E)$ for the pristine, alloyed, and heterostructured NRs having seven layers (indexed by n and/or m) are shown in Fig. 2 (a). A comparison with the pristine NRs reveals

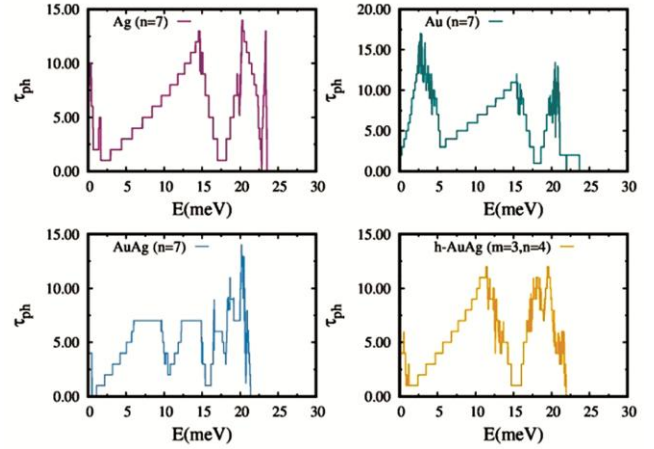


Fig. 2 – The phonon transmission coefficient τ_{ph} plotted as a function of phonon energy E for the pristine, alloyed, and heterostructured NRs.

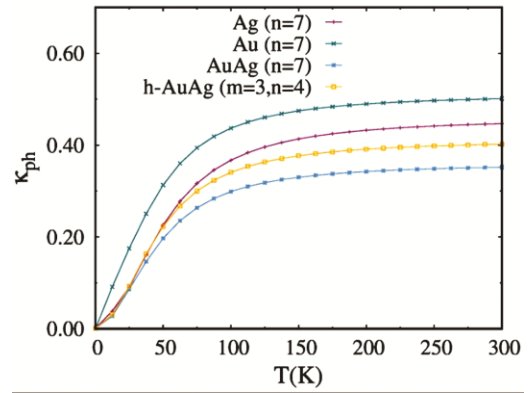


Fig. 3 – The phonon thermal conductance k_{ph} plotted as a function of temperature T for the pristine, alloyed, and heterostructured NRs.

that the Debye energy (the maximum energy a phonon can have) is reduced in the alloyed and heterostructured NRs, with the former exhibiting the maximum reduction. The number of conduction channels available for phonon transport also decreases in both alloyed and heterostructured NRs. This decrease is more pronounced in the alloyed NRs, particularly in the low energy region.

Figure 3 depicts the variation of k_{ph} with temperature T for the pristine, alloyed, and heterostructured NRs. In all three systems, k_{ph} rises with increasing T , before saturating to a system-specific constant value at T around Debye temperature). However, quantitatively there is a significant difference in k_{ph} with respect to the pristine NRs. As an interesting result, it is found that both alloying and hetero-structuring result in a significant reduction of k_{ph} over the pristine NRs, with alloyed

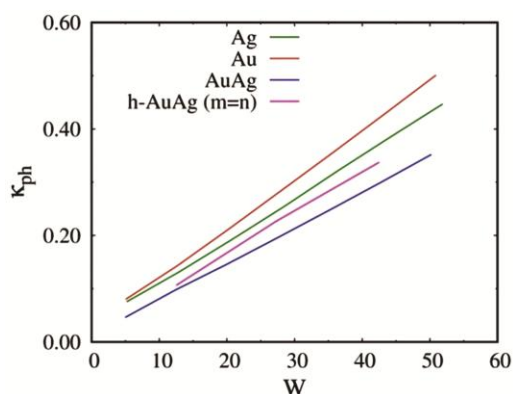


Fig. 4 – The phonon thermal conductance k_{ph} plotted as a function of Width W (Å) for the pristine, alloyed, and heterostructured NRs.

NRs having the least value of k_{ph} . At room temperature, the alloyed NRs show a reduction of about 25% over the average k_{ph} of the pristine Au and Ag NRs. This is an important prediction from the point of view of thermoelectricity.

Further, we explore the dependence of k_{ph} on the width W of the NR. Figure 4 displays the room-temperature k_{ph} as a function of W for the pristine, alloyed, and heterostructured NRs. As for the pristine NRs, k_{ph} is found to increase linearly with W for the alloyed and heterostructured NRs. Over the investigated range of W , k_{ph} for the alloyed NRs lies at the bottom among the considered NRs.

4 Conclusions

In summary, we have computed the phonon thermal conductance k_{ph} for the alloyed and heterostructured NRs of Ag and Au by using the GULP code together with the non-equilibrium Green's function approach. We find that both alloying and hetero structuring provides an important means to suppress k_{ph} , with alloying having a relatively more pronounced effect. At room temperature, the alloyed NRs show a reduction of about 25% over the average k_{ph} of the pristine Au and Ag NRs. This constitutes an important finding of our study as it is desirable in thermoelectric generation to have as small k_{ph} as possible. Materials with low thermal conductance, but at the same time high thermoelectric power, have high thermoelectric efficiency. It would therefore be interesting and important to investigate the effect of alloying and hetero structuring on the electronic part of thermal conductance and thermoelectric power of NRs. Work in this direction is currently under progress.

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