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Highlight

Metavalent bonding impacts charge carrier transport across grain boundaries

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ABSTRACT

Understanding the mechanisms underpinning the charge carrier scattering at grain boundaries is crucial to design thermoelectrics and other electronic materials. Yet, this is a very challenging task due to the complex characteristics of grain boundaries and the resulting difficulties in correlating grain boundary structures to local properties. Recent advances in characterizing charge transport across grain boundaries are reviewed, demonstrating how the microstructure, composition, chemical bonding and electrical properties of the same individual grain boundary can be correlated. A much higher potential barrier height is observed in high-angle grain boundaries. This can be ascribed to the larger number density of deep trapping states caused by the local collapse of metavalent bonding. A novel approach to study the influence of the local chemical bonding mechanism around defects on the resulting local properties is thus developed. The results provide insights into the tailoring of electronic properties of metavalently bonded compounds by engineering the characteristics of grain boundaries.

KEYWORDS

metavalent bonding, charge carrier scattering, grain boundary, thermoelectric

Grain boundaries (GBs) influence the transport of mass, heat, and charge. The study of GBs and their influence on the properties of materials is thus a significant and burgeoning topic. Charge transport across GBs impacts the electrical loss of transmission lines [1], potentially reduces the quantum efficiency of solar cells [2], and provides optimization potential for thermoelectrics [3]. Thermoelectric materials can realize the interconversion between thermal energy and electricity, providing sustainable clean power generation, for example, from omnipresent heat sources [4, 5] and even sunlight [6], as well as site-specific active cooling for on-chip thermal management [7, 8]. The thermoelectric energy conversion efficiency is determined by a figure-of-merit, $zT=S^2\sigma T/(\kappa_e+\kappa_l)$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, κ_e is the electronic thermal conductivity, and κ_l is the lattice thermal conductivity [9]. These intertwined parameters place an obstacle to the improvement of zT. Grain boundary engineering, i.e., by modifying the GB number density, microstructures, and compositions, has been considered an effective avenue to decouple the tradeoff between these thermoelectric parameters. For example, a high density of twin boundaries [10] or low-angle GBs [11] has caused a significant reduction in κ_l while keeping reasonably high electrical conductivity. In contrast, the electrical conductivity is seriously degraded by reducing the grain size with randomly oriented GBs, which even counteracts the beneficial effect of reduced κ_l by GB phonon scattering [12, 13]. This dichotomy of the detrimental and beneficial effects of GBs on thermoelectric performance requires explanations based on a microscopic understanding of the relevant phenomena.

However, GBs are ubiquitous microstructures in polycrystalline samples characterized by several quantities. Besides the five macroscopic degrees of freedom describing the orientation of the GB [14], additional characteristics such as the GB free volume, distribution of dopants, and the chemical bonding mechanism are also indispensable to understand GB properties. The majority of studies on GB effects rely on controlling grain size [1, 12, 13, 15]. Recent work also demonstrates that GB complexions and GB precipitates impact the thermoelectric properties differently [16]. Nevertheless, these conclusions are based on the transport properties of bulk polycrystalline samples that average the influence of individual GBs. The mechanisms underpinning the controversial phenomena for the increased and decreased zT by shrinking the grain size are still elusive. It seems that correlating the microstructures, compositions, and chemical bonding mechanisms with the local electrical conductivity of an individual GB is a prerequisite to unravel the complexity of charge transport across GBs.

In a recent publication in *Nature Communications*, Wu et al. [17] developed a novel correlative method to reach this goal. They investigated the microstructures characterized via electron

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backscatter diffraction (EBSD) (Fig. 1(a)), and determined the charge carrier transport across a single GB with a physical property measurement system (PPMS) (Fig. 1(b)). Finally, the local chemical bonding mechanism was revealed by atom probe tomography (APT) [18]. This suite of approaches enables the authors to measure the temperature-dependent charge carrier mobility for trace Ag-doped PbTe samples with various GB misorientation angles, as shown in Fig. 1(c). Note that each lamellar sample only contains one single GB. Under the reasonable assumption that the scattering of GBs and grain interior is uncorrelated, the impact of GBs on the carrier mobility can be determined by $\mu_{GB}^{-1} = \mu^{-1} - \mu_G^{-1}$, where μ_G is the mobility of the single-grain sample [19]. The GB potential barrier height (E_b) can thus be derived employing an Arrhenius-type thermal excitation process for charge carriers overcoming a potential barrier at the GB [20]. Figure 1(d) illustrates that the potential barrier height for high-angle grain boundaries (HAGBs) is 4–5 times larger than that for low-angle grain boundaries (LAGBs). The GB potential barrier can be described using a trapping state model as $E_b = (e_2 Q_t^2)/(8N\varepsilon_{st})$ [21]. Here, the trapping state density (Q_t) and the static dielectric constant (ε_{st}) are responsible for different E_b values of different GBs.

In general, it is quite challenging to experimentally measure these two parameters. Wu et al. [17] found that they can both be qualitatively described based on the APT data. As shown in Fig. 1(e), the LAGB is composed of dislocation arrays with a lower segregation degree of Ag dopants. In contrast, the HAGB is fully covered by dopant atoms with a higher segregation degree. This corresponds to a larger number density of Q_t at the HAGB, which is partly responsible for the higher GB potential barrier height. The static dielectric constant is the low-frequency limit of the dielectric function, describing the response of a material to an applied electric field. This parameter depends on the polarizability of valence electrons and thus the chemical bonds. It has been shown that a large dielectric constant is characteristic of metavalently bonded materials due to the large overlap of p-orbitals that delocalize electrons [22]. The metavalent bonding mechanism of the PbTe sample studied in this work is closely related to the high value of the "probability of multiple events" (PME) [23], i.e., an unconventional bond rupture in APT. Strikingly, the PME value drops significantly within the dislocation cores and the whole plane of the HAGB (Fig. 1(f)), indicative of a local breakdown of metavalent bonding. This collapse of metavalent bonding at HAGBs locally decreases the dielectric constant, which results in a weakened dielectric screening ability and an increased GB potential barrier height.

It is worth highlighting that the influence of trapping states on the charge scattering at GBs has been recognized for decades, yet, the impact of local chemical bonding transition has only been revealed recently. More importantly, metavalent bonding is a bonding mechanism that prevails in a class of materials, which show a combination of properties [24] favorable for thermoelectrics [25], phase-change memories [26], topological insulators [27] and photovoltaics [28]. The *Nature Communications* study demonstrates that changes in bonding at grain boundaries can be utilized to tailor the properties of such advanced functional materials.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

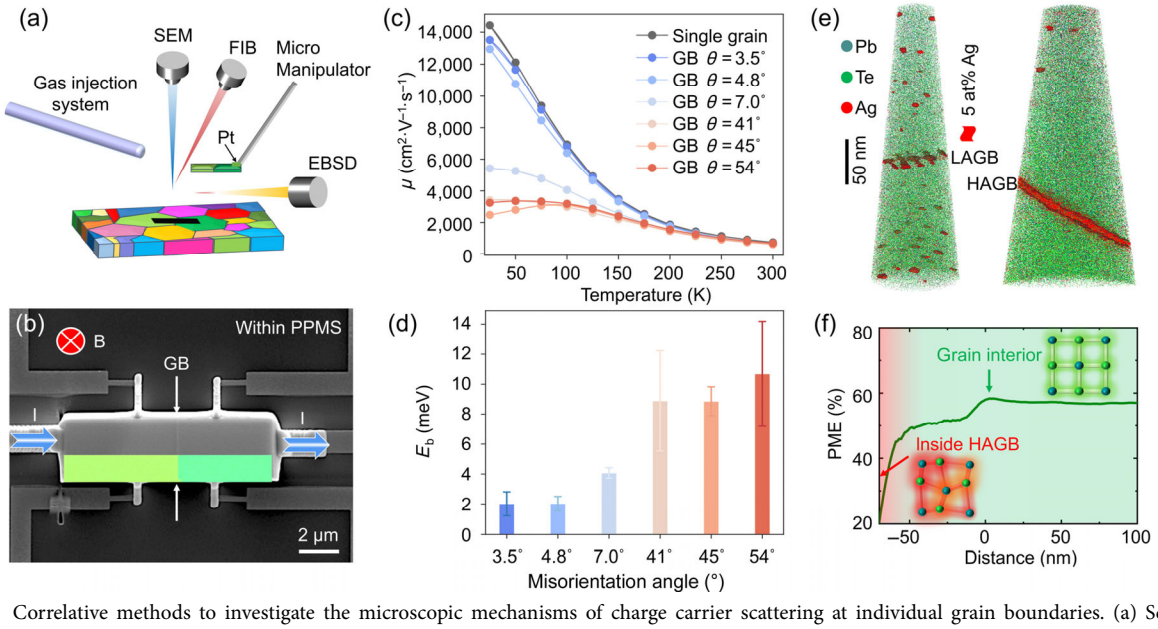

Figure 1 Correlative methods to investigate the microscopic mechanisms of charge carrier scattering at individual grain boundaries. (a) Schematic diagram illustrating the fabrication process of individual GB devices. (b) A hall-bar geometry sample mounted on a micro-scale measurement device with electrodes prepared by electron-beam lithography. (c) Temperature-dependent carrier mobility for samples with individual GBs that differ in misorientation angles. (d) Histogram of the GB potential barrier height showing the increased charge carrier scattering at GBs from LAGBs to HAGBs. The error bars were determined by varying the cut-off data points for linear fitting. (e) Atom probe tomography investigation of two specimens including individual LAGB (left) and HAGB (right). The iso-composition surfaces of 5 at.% Ag depict the Ag-decorated dislocation arrays at a LAGB and the Ag fully covered HAGB. (f) PME profile shows a significant drop of PME inside the HAGB while remaining at a relatively high value in the grain interior. Figures are adapted with permission from Ref. [17], © R. G. Wu, et al. 2023.

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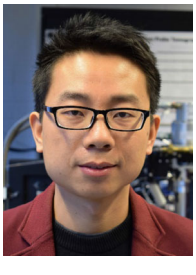

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