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EDITORIAL

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A method for the direct measurement of chemical bonds

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The development and application of advanced materials are changing human society. The performance of materials directly determines their applications. The properties of materials intrinsically rely on their microstructures and chemical bonds. For designing the desired properties, a profound understanding of the microstructure-chemical bond-property relationship is of significant. Therefore, the characterization of microstructures and chemical bonds represents one of the fundamental themes in material science.

Techniques for characterizing the microstructure of materials are relatively mature. Scanning electron microscopy (SEM) enables the observation of micro-morphology, and electron backscattering diffraction (EBSD) reveals the crystal orientations and the grain boundary distributions. High resolution scanning transmission electron microscopy (STEM) represents the atomic level image, while elemental energy spectrum (EDS) demonstrates the accurate composition. Atom probe tomography (APT) provides three-dimensional atomic-level compositional distributions, which takes special advantages of studying interfaces and nanoclusters, etc. In contrast, direct characterization of chemical bonds is more challenging. Currently, the primary approach relies on vibrational spectroscopy techniques such as fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy to indirectly analyze the bond properties, while X-ray photoelectron spectroscopy (XPS) probes electronic states via chemical shifts. Theoretical calculations such as density functional theory (DFT) can predict bond energies, bond length and bond angle. However, due to the dynamic nature of chemical bonds and complex interactions, direct experimental observation of such bonds still remains challenging.

APT has emerged as a well-established technique for three-dimensional compositional analysis of materials at the atomic scale. Prof. Matthias Wuttig and his team from RWTH Aachen University in Germany has demonstrated its potential for localized chemical bond characterization. The principle of atom probe tomography (APT) relies on field evaporation—the process by which charged atoms (ions) are ejected from the sample surface under a high electric field of ≈10^{10} V m^{-1}. Combining time-of-flight mass spectrometry and position-sensitive detectors, they together reconstruct the 3D distribution of elements with subnanometer-scale spatial resolution. It is well-accepted that in an atom probe experiment, both atomic and molecular ions are field-evaporated and registered by a position-sensitive detector. However, only in specific materials can fragments be dislodged from the tip as molecular ions, thus suggesting that the release of molecular ions in laser-assisted field evaporation is characteristic of specific bond breakage[1,2]. Define this probability as PMI, i.e., the probability of molecular ionization (Figure 1a). In addition, some materials may have multiple ion signals detected under a single successful pulse during an APT testing, i.e., multiple events occurring, which is likewise characteristic of specific bond breakage. Define this probability as PME, i.e., the probability of multiple events (Figure 1b)[3].

The working principle of APT, which relies on field evaporation, allows us to understand various bond breakage scenarios. Field evaporation requires an electric field large enough to break the bonds between a surface atom and its neighbors, thus enabling the atom's removal from the material[4]. On this surface, a certain density of electrons is generated in response to the external field. These surface charges shield the electric field, and the greater the charge density, the smaller the field penetration depth. The depth of the field penetration is closely related to the formation of molecular ions. For metals, the field screening effect is so significant that the field penetration depth is much lower than the interatomic spacing, resulting in no molecular ions being formed upon laser-assisted field evaporation. For all other solids, both covalent and metavalent, the field penetration length is greater than the interatomic spacing, which is sufficient to produce molecular ions. It is worth noting that there are regions with particularly large values of field penetration depth in the transition from metals to covalent solids, i.e., the region where metavalent solids are. This further evidence that metavalent bonding is indeed another unconventional bonding mechanism.

Three different scenarios of bond breakage can be successfully distinguished using these two probability values, as shown in Figure 1c. Solids like Al, Au, Ag, Cu, W, and NiAl present a very low PMI and a low PME which apparently demonstrate the characteristic of metals. On the contrary, solids like GaAs, GaSb, or InSb, have a much higher PMI while the PME is low. This bond breakage scenario is characteristic

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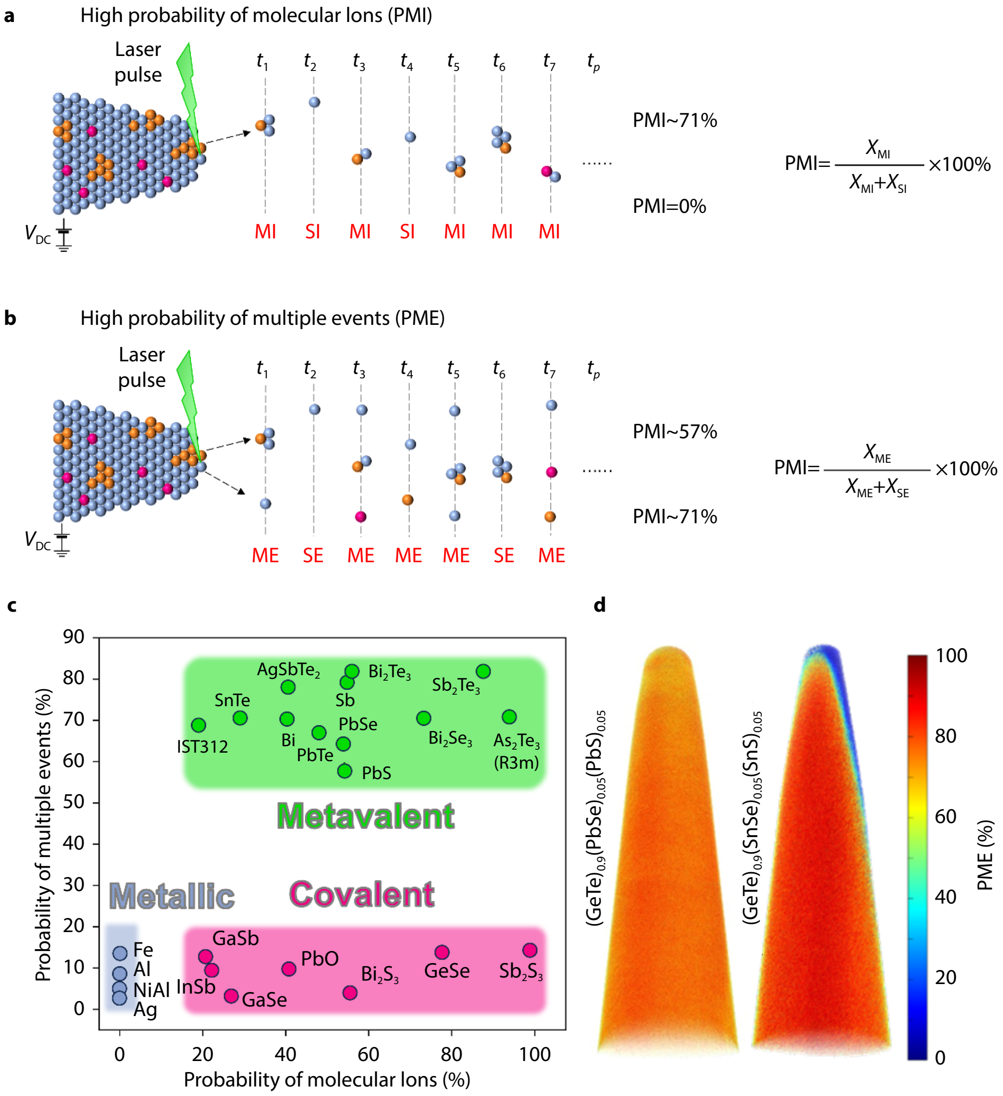

Fig. 1 Schematic diagram of APT localized chemical bond characterization. **a** Sketch of a bond-breaking experiment for a sequence of successful pulses exhibiting high PMI, as well as **b** a sketch of the same experiment exhibiting high PME. SI and MI respectively stand for a single ion and molecular ions, while SE and ME respectively stand for a single event and multiple events to be dislodged upon bond rupture. **c** Demarcation of different chemical bonding mechanisms by PMI and PME: metals (in blue), metavalent solids (in green), and covalently bonded compounds (in red). **d** The corresponding bonding mechanisms of $(GeTe)_{0.9}(PbSe)_{0.05}(PbS)_{0.05}$ and $(GeTe)_{0.9}(SnSe)_{0.05}(SnS)_{0.05}$ are revealed by 3D PME maps characterized by APT.

of covalent materials. Besides, a significant number of chalcogenides show yet another characteristic bond rupture. These solids, like GeTe, Sb_2Te_3, PbTe, or Bi, have unusually high PME values of above 50%, and PMI values much higher than metals. This type of bond breakage indicates an unconventional bonding mechanism that differs from classical covalent, ionic, and metallic bonding, termed metavalent bonding (MVB)[5].

The MVB mechanism has shown great potential for designing the nucleation and crystallization kinetics of phase-change materials, as well as the electron and phonon transport of thermoelectric materials[6–11]. For example, in thermoelectrics, Dr. Yuan Yu boosts the thermoelectric performance for GeSe, SnTe, GeTe, and other materials by the design of MVB[6,9,11], and demonstrates that the 3D PME maps characterized by APT show the distribution of localized chemical bonds, which facilitates suitable dopant selection, as shown in Figure 1d.

The expansion of APT applications in localized chemical bond characterization and the proposed mechanism of MVB represent a significant breakthrough in materials science, yet several fundamental and applied challenges remain. First, although it has been shown that differences in the field penetration depth cause bonds to fracture in different ways, it is still unclear what properties of materials are related to differences in the field penetration depth. How to leverage this property to guide the design of chemical bonds in materials remains a question worthy of investigation. Second, the intrinsic mechanism behind the similar PMI values for covalent and metavalent, but the large difference in PME, remains unclear. Third, how to use APT to characterize other bond types, such as ionic bonds. It is believed that the application of APT will be more complete with further research and play a greater role in materials science.

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DECLARATION OF COMPETING INTEREST

There are no conflicts to declare.

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