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Investigation of the van der Waals epitaxy gap in isostructural semiconducting germanium tellurides: $HfGeTe_4$ and $ZrGeTe_4$

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ABSTRACT

Two isostructural semiconducting germanium tellurides: $HfGeTe_4$ and $ZrGeTe_4$ have been investigated for the van der Waals epitaxy gap existing between layers of atoms using the charge density route. The Maximum Entropy Method (MEM) is used for the reconstruction of the charge density derived from the XRD information. 3-dimensional charge density maps visualize the van der Waals epitaxy gap, while 2-dimensional and 1-dimensional charge density maps and profiles have been picturised and quantified for the localized charges between the atoms, especially in the valence region. The types of bonding existing are identified, and the strength of the bonds is quantified in order to identify the weak van der Waals and strong covalent, metallic bonds which exist in the chosen systems. The charge density and van der Waals epitaxy gap in both systems reveal the fact that $HfGeTe_4$ is more fragile than $ZrGeTe_4$.

1. Introduction

An increasing number of ternary tellurides have been synthesized and characterized by Mar et al. and others [1–5] in the early 1990’s. New ternary semiconducting chalcogenides, zirconium germanium tetra telluride ($ZrGeTe_4$) and hafnium germanium tetra telluride ($HfGeTe_4$) have been synthesized and their structures have been determined by X-ray diffraction methods [6]. The compounds $ZrGeTe_4$ and $HfGeTe_4$ are semiconductors and are non-stoichiometric with orthorhombic structure having a space group of $Cmc2_1$. Also, they are isostructural and they adopt new layered structure types, in which the basic structural building blocks are metal centered bicapped trigonal prisms, as shown in Fig. 1a and 1b, one of whose caps is a $GeTe_3$ trigonal pyramid. The structure of $MGeTe_4$($M = Zr$, Hf) consists of true two-dimensional layers of [$MGeTe_4$]; its details have been elaborated by Mar et al. [6].

The ternary group IV metal germanium chalcogenides are of chalcogen-poor phases MGeQ($M = Zr$, Hf; $Q = S$, Se, Te) [7,8] which adopt the PbFCl structure type. In these compounds, there is no ambiguity about the role that the Ge atoms play. They behave, together with the Q atoms, as anions that coordinate around the metal cation in a tricapped trigonal prismatic fashion. In the tellurium phases MGeTe, one of the capping Te atoms is sufficiently distant that the metal atoms should properly be considered to be in a bicapped trigonal prismatic environment. The only known ternary group V metal germanium chalcogenide is $Nb_3Ge_xTe_6$, $x = 1$ [9], $x = 0.9$ [10]. Their structure contains Nb-centered trigonal prisms, whose

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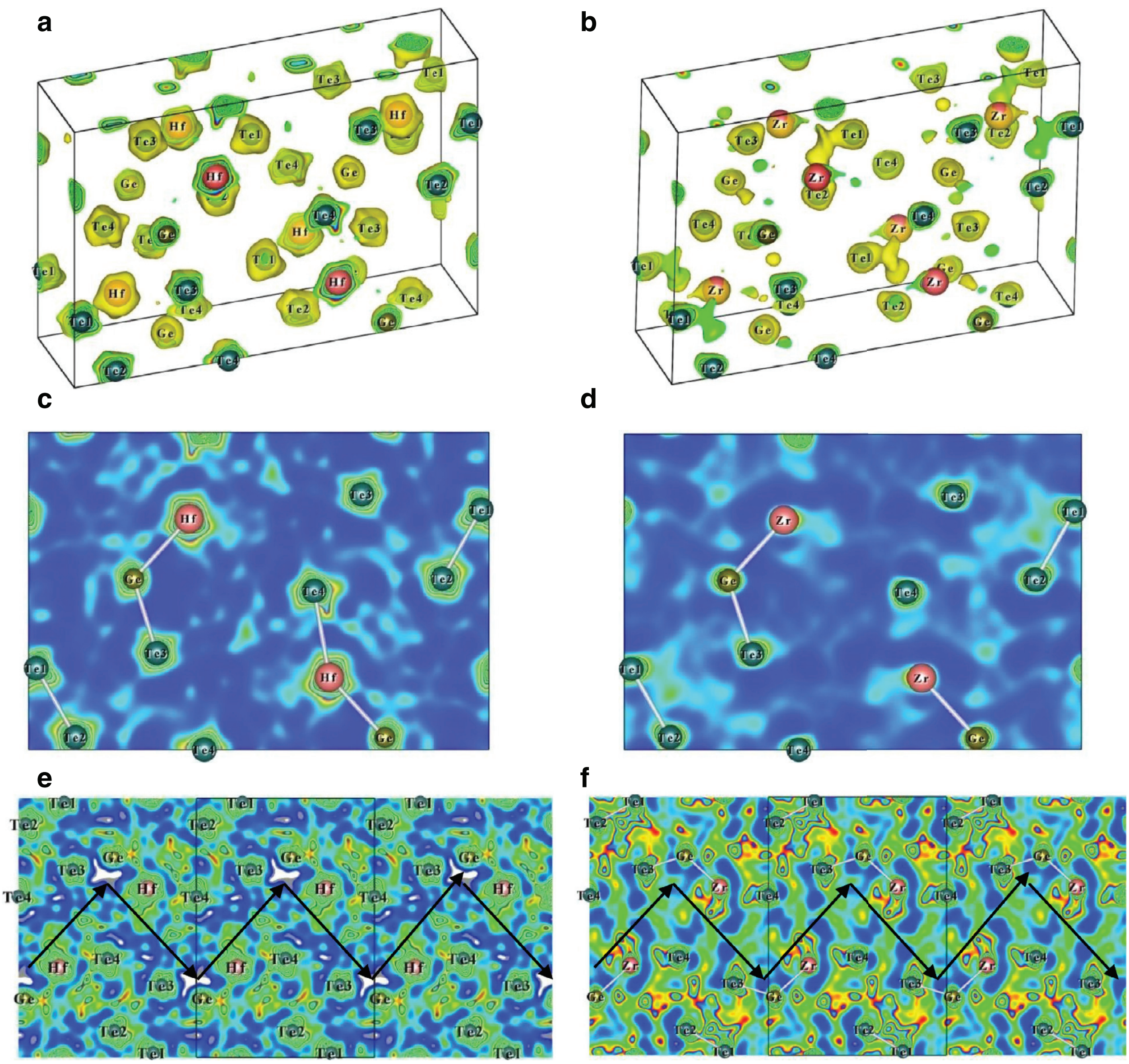

Fig. 1. 3-Dimensional charge density in the unit cell of HfGeTe4 and ZrGeTe4 and Two dimensional variation of charge density along selected planes at the isosurface level of 0.05e/Å^3 (for Fig. 1e and 1f).

rectangular faces are capped by Ge and neighboring Nb atoms. The Ge atoms in turn are coordinated by Te atoms in a distorted square-planar fashion.

Black crystals of the ternary compounds like HfGeTe$_4$ and ZrGeTe$_4$ generally grow as flat needles that are very thin and easily bent due to the layered nature of the structures. The compound ZrGeTe$_4$ is particularly prone to form as hair-like fibers. The products are invariably contaminated with binary compounds. The semiconductor behavior of these type of materials are mainly due to Anderson localization [11] owing to the randomness introduced by the Zr vacancies and the relaxation of the Te positions around these vacancies. Vacancies in the Zr position can actually lead to the reduction of the charge density at an atomic site, and this will lead to a localization of charges in the mid bond region which is a characteristic of semiconductors.

The generally lower absolute conductivities ($\sigma_{300} = \sim 10\ \Omega^{-1}\mathrm{cm}^{-1}$) and the wider saturation region in HfGeTe$_4$can be attributed to the lower purity and the deficiency of Hf that can be found from the crystal structure determination of HfGeTe$_4$. The deficiency in Hf and the vacancies produced in a crystal can produce acceptor levels that mimic the effects of impurity doping [12], and this results in band gaps of 0.11 and 0.18 eV calculated for ZrGeTe$_4$ and HfGeTe$_{4,}$ respectively.