

Studies of interfaces and amorphous nano-volumes – RDF analysis and HAADF imaging using an aberration corrected TEM/STEM

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As structural components of devices and materials become smaller in size, there is increasing interest in developing capabilities to analyse not only nano-volumes of crystalline phases but also amorphous nano-volumes and the interfaces between the amorphous and crystalline phases. In this paper, we report two parallel approaches to this problem – methods for investigating the structure of small volumes of amorphous materials by reduced density function (RDF) analysis, and HAADF imaging of crystalline-amorphous interfaces.

RDF analysis of amorphous nano-volumes. The technique of electron energy selected RDF analysis was originally developed to study thin films [1], but recently it has been extended to volumes approaching 1 nm in width [2]. This allows local variations in structural order to be studied, for example in intergranular films, amorphised volumes (e.g. in DVDs) and barrier layers. While the resulting data, can be interpreted straightforwardly for elemental systems (e.g. a-C, a-Si), the interpretation is less straight forward for alloys. One method is to use $G(r)$ as a data set against which to refine the $G'(r)$ obtained from a model structure. $G'(r)$ can be obtained by calculating the diffraction pattern from the model, and then refining the model (e.g. Monte Carlo refinement) to achieve $G'(r) = G(r)$. The resulting model will not be unique, and constraints must be applied (e.g. energy constraints, restricting atomic displacements) if unphysical models are to be avoided. An example of refining $G(r)$ against $G'(r)$ is shown in figure 1, obtained from thin film $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (used in rewriteable DVDs).

HAADF imaging of IGF films in Si_3N_4 ceramics. Rare-earth elements are used as sintering aids in the production of Si_3N_4 ceramic components. They promote the growth of thin, needle-like grains [3] which give high toughness and strength [4]. Different rare-earth additions produce different outcomes e.g. for crystals grown in a glass matrix [5], La additions result in an average grain aspect ratio five times that shown by samples containing Lu. In this study, we have determined, for the first time, the three-dimensional arrangement of rare-earth atoms extending into the amorphous phase (both intergranular films and pockets) at the prismatic interfaces, in Si_3N_4 containing La, Sm, Yb and Lu using aberration-corrected high-angle annular dark-field scanning transmission electron microscopy [6] (HAADF-STEM).

HAADF-STEM images were obtained using a unique JEOL 2200FS TEM/STEM fitted with aberration-corrected probe-forming and objective lenses. The periodically averaged HAADF-STEM images of *grain-intergranular film* interfaces are shown in the upper row of Fig. 2 for all four rare-earth dopants, viewed parallel to mutually perpendicular [001] and [100] directions. Immediately below the upper row of images in Fig. 2 are images from the analogous *grain-glass pocket* interfaces. The Si_3N_4 crystal terminates as a row of half-hexagons when projected parallel to [001]. The structure beyond the row of half-hexagons is likely to represent rare-earth atoms in preferred positions in the amorphous phase. Up to five inequivalent preferred positions were observed (e.g. Sm, see Fig. 2) parallel to [001]. These positions are the same (within experimental error) independent of whether the interface was that of a grain-intergranular film or a grain-glass pocket. The third atomic coordinate of the preferred atomic positions, which is not available from [001], is obtained from the images parallel to [100]. While the atomic arrangement in the amorphous phase conforms to the periodicity of the terminating crystal plane in all four cases, the attachment sites are very

different for the different additive rare earth species. The atomic positions in the amorphous phase are presented as distances from a defined origin in the crystalline phase, and are determined to within ~ 0.02 nm in three dimensions [submitted for publication].

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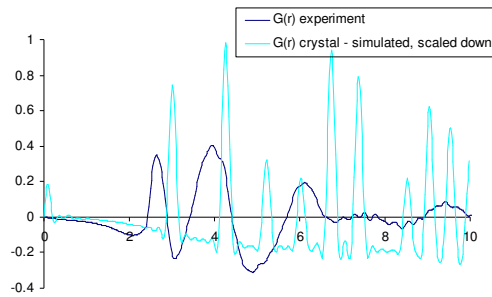


Fig 1a $G'(r)$ of the NaCl type crystal (structure shown at right) in comparison with the experimental data recorded from an amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ layer. r is given in Angstrom and the units on the second axis ($G(r)$) are arbitrary.

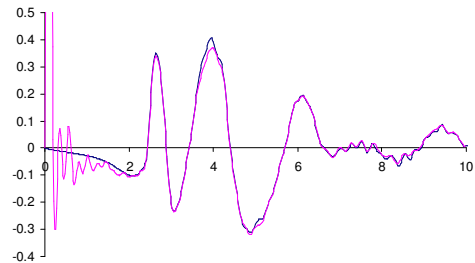
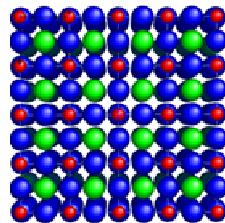


Fig 1b Experimental $G(r)$ and the refined $G'(r)$ when taking a NaCl type crystal as a starting model. r is given in Angstrom and the units on the second axis are arbitrary. The resulting (refined) amorphous structure is shown at right.

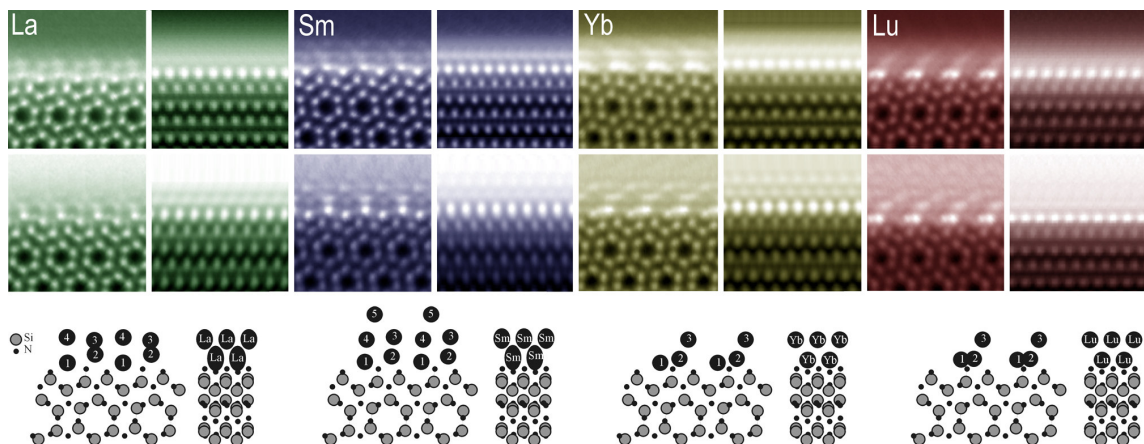
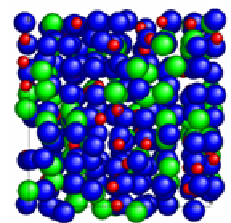


Fig. 2. Averaged images of both grain-intergranular film interfaces (upper row of images) and grain-glass pocket interfaces (immediately below upper row of images). For each rare-earth additive (La, Sm, Yb, Lu), images represent the projected structure parallel to both $[001]$ (left) and $[100]$ (right). The schematic representation of the atomic positions of all species is indicated.