

Fivefold Twinning in Nanosized Particles and Nanocrystalline Thin Films – Ubiquitous Metastable Structures

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Abstract

Fivefold twinning in thin films and small particles of nanometer dimensions is the origin of metastable structures the ubiquitous presence of which in a whole class of nanocrystalline materials results from the great variety of materials and fabrication processes involved. These are reviewed and discussed together with the formation mechanisms of such structures and their stability including the role of lattice defects. Various illustrative examples are aimed to emphasise the importance of this phenomenon in the area of nanocrystalline materials.

1. Introduction

One important advantage of making nanocrystalline materials are the low temperature routes of synthesis becoming accessible. Under such conditions not only the formation, but also the stability of so formed intermediate range structures are governed rather by medium range ordering and surface/interface energy minimization than by fast diffusion and far reaching forces. These processes frequently result in metastable structures which for a whole class of materials most commonly are fivefold twinned [1].

Fivefold twinning denotes repeated twin formation on alternate coplanar twin planes so as to form circular arranged, wedge shaped twins sharing a common axis of fivefold symmetry. Preferentially, face centered cubic (fcc) or diamond cubic (dc) crystals, having low twin boundary energy, are concerned. Fivefold twinned structures are composed of tetrahedral subunits joined together on adjacent bounding faces being first order twin planes (mirror planes) of the respective crystal that enclose an angle of about $2\pi/5$.

Two types of multiply twinned particles (MTP's) may be formed according to the above construction scheme: *i.* decahedra (pentagonal bipyramids), composed of five tetrahedral subunits sharing one fivefold axis, bounded by 10 triangular faces; *ii.* icosahedra with six fivefold axes, composed of 20 tetrahedra sharing one common point at the centre, bounded by 20 triangular faces. As tetrahedral subunits of regular fcc or dc lattice cannot form space filling structures there remains an angular misfit resulting in serious issues with respect to their stability.

Multiple twinning in crystalline solids of nanometer dimensions is known since the early work of J. Segall [2]. More than forty years study in this field have revealed the ubiquitous presence of such metastable, fivefold twinned structures for a huge number of low-dimensional materials of various origin and nature. Being concerned with the main issues of fivefold twinning, i.e. materials and processes involved, formation mechanisms, and stability and lattice defects, respectively, this contribution will present various illustrative examples obtained by high resolution electron microscopy (HREM) and discuss their relevance for the art and science of making nanocrystalline materials.

2. Materials and processes

In principle, fivefold twinned structures may be found in any crystalline material which allows twinning on alternate coplanar twin planes enclosing an angle of about $2\pi/5$. Mostly, cubic crystals are concerned which exhibit a surface energy anisotropy so as to favour shapes deviating from the single crystalline cuboctahedron. Experimental proof of this has been obtained up to now for Fe, Co [3,4] and most of the fcc transition metals, i.e. Ni, Cu, Rh, Pd, Ag, Pt and Au [2,3,5-13], and for the group IV dc crystals of C, Si and Ge [14-21], respectively. Structures like that of the decahedral MTP of Rh shown in Fig. 1 [13] are characteristic for the above materials. The number of multiply twinning in elemental materials is completed by the group III hexagonal close packed Mg [22] and the lanthanides Sm [23] and Yb [24]. Only very recently, MTP formation for fcc Al was achieved by electron beam induced decomposition of θ -Al₂O₃ [25]. This long expected result, obtained mainly by preventing surface oxide formation during nucleation and growth of the Al particles, points to the important role of the surface in such processes.

Fivefold twinned structures not only occur in elemental crystals, but also in cubic modifications of binary and ternary halides, nitrides, carbides and oxides, as BN [26], TiN [27], TiCN [28], SiC [29], Fe₂O₃ [30] and BaTiO₃ [31], metal alloys, as Au-Cu and Au-Fe [32,33], and compound semiconductors AgBr [34], GaP [35], CuInSe₂ [36] CdTe [37], respectively. The summary of materials must be completed by the molecular crystal fullerite (C₆₀), the material from which the up to now largest MTP's are known [38], and by composite materials like Ge precipitates in Al alloys [39] or Ag precipitates in glasses modified by ion exchange [40], respectively. The multitude of aspects of fivefold twinning, belonging to the "Preferred Structures in Small Particles" [41], very recently was further extended to self-assembled nanocrystal superlattices [42].

The processes and specific techniques by which multiply twinned structures in small particles and thin films are generated include synthesis *i.* from the vapour phase, *ii.* from the liquid phase, and *iii.* from the solid phase, respectively. The first point (*i.*) concerns (a) heterogeneous nucleation and growth of particles and thin films on substrates, and (b) homogeneous nucleation and growth of particles in a gas stream. Most of the early work on metal MTP's [5-7] have been done according to the process scheme (a) by thermal evaporation and condensation of metal vapour on insulating sub-

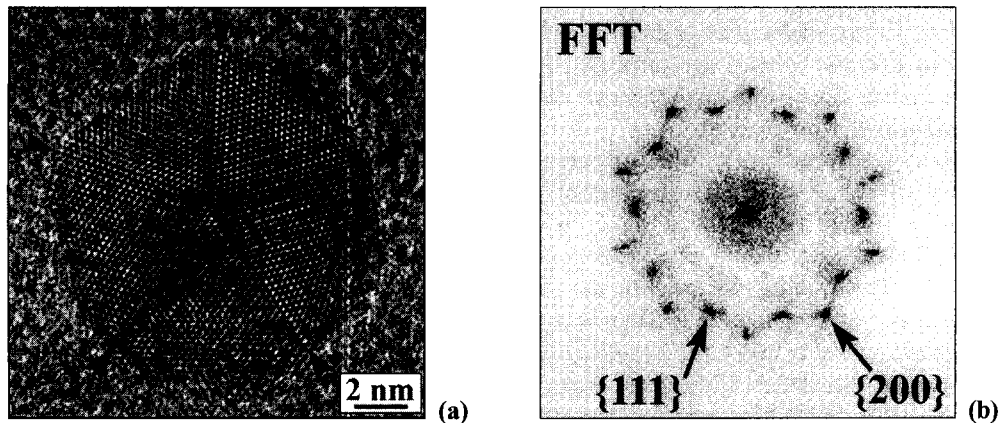


Fig. 1: HREM image (a) and diffractogram (b) of a decahedral MTP of Rh grown by nucleation from the vapour phase. The twin boundaries marked by arrow heads meet at the fivefold axis perpendicular to the image plane. The reciprocal space representation (FFT) illustrates by the arrangement of {111} and {200} spots the fivefold symmetry of the particle.

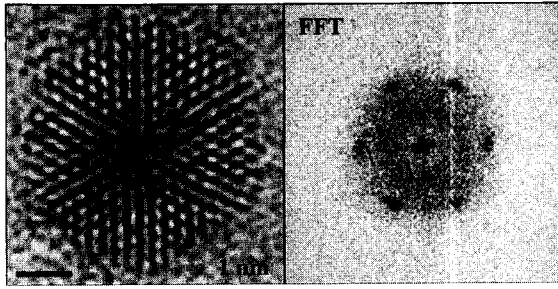


Fig. 2: Icosahedral MTP of Ag, left: HREM image, right: diffractogram, grown by sol-gel synthesis of a Ag/SiO₂ nanocomposite, imaged in threefold symmetry orientation. The contrast of lattice plane fringes and the spot splitting in the FFT are characteristic of the angular misalignment of twinned subunits.

strates. In thin film formation, e.g. of diamond [43] mostly chemical vapour deposition from precursor molecules is utilized. The process scheme given in (b) frequently is used for mass production of particulates [8] and for in-situ investigations [44].

The second point (ii.) includes (a) growth from the melt and (b) precipitation and deposition by chemical or electrochemical reduction of salts in solutions. Melt grown fivefold twinned grains have been reported for Si and Ge [15] and solution grown MTP's for AgBr [34]. Metal colloid precipitation by reduction of metal salts from solutions frequently is used for wet chemical

synthesis of transition metal particles [45], including also sol-gel synthesis of metal oxide nanocomposites [46] from which Fig. 2 shows an example. Electrodeposition mainly is applied for protective metal (mostly Ni) coatings, [47]. Fivefold twinned grains [48] are the main constituents in films with $\langle 110 \rangle$ texture formed by appropriately choosing the coating conditions.

The third point (iii.) includes (a) precipitation from solid solutions in crystalline and glassy hosts and (b) solid phase crystallisation from the amorphous phase. Fivefold twinned rods of Ge precipitated upon thermal treatment from Al/Ge alloys [39] and multiply twinned metal particles precipitated from glasses modified by ion exchange or ion implantation [40,49] (see Fig. 3) are examples of the process scheme (a). The amorphous-to-crystalline phase transition according to process scheme (b) has been studied intensively for thin films of Ge [19,20] and small particles of Si [21] which exhibit a distinct tendency to fivefold twinned structure formation.

4. Formation mechanisms

Because of the great variety of materials and processes involved it is quite obvious that they cannot be attributed to one uniform mechanism of formation. In general, one can distinguish three different formation mechanisms: *i.* by nucleation and layer-by-layer growth, *ii.* by successive growth twinning, and *iii.* by deformation twinning.

Magic numbers in the mass spectra of transition metal cluster beams indicate the preferred formation of closed shell structures with icosahedral shape [50]. Such clusters may evolve from 13 atoms icosahedral nuclei maintaining their shape by layer-by-layer growth so to arrive at particles with sizes of several nanometers. Accordingly, pentagonal decahedra may evolve from 7 atoms nuclei of decahedral shape. During growth the non-crystallographic packing of atoms of the nucleus readily is transformed to a fivefold twinned arrangement of translationally ordered units the small size of which easily enables compensation of angular misfits. The examples shown in Figs. 1 - 3 are considered to result from this formation mechanism.

According to their bonding characteristics in dc materials a 20 atoms dodecahedron and a 15 atoms truncated pentagonal bipyramid may serve as icosahedral and decahedral nuclei, respectively. Such clusters are believed to be effective in the nucleation of fivefold twinned structures in diamond [17] and Ge thin films [19]. A more extended cluster of 100 atoms (based on a 20 atoms core of dodecahedral shape, the 12 pentagonal faces of which are decorated by truncated pentagonal bipyramids) is proposed as prototype of clusters formed in the plasma enhanced CVD of amorphous Si particles

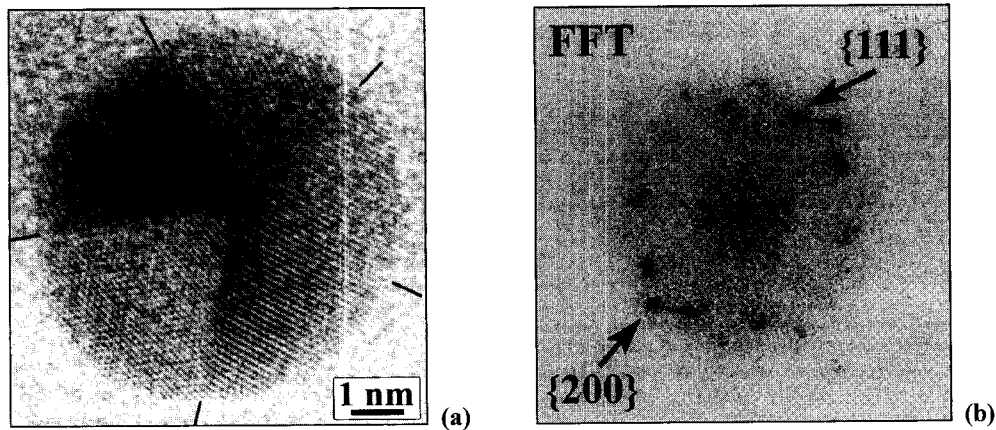


Fig. 3: HREM image (a) and diffractogram (b) of a decahedral MTP of Ag grown by thermally induced redox reaction of silver ions incorporated into glass by ion exchange. The particle slightly tilted out of perfect fivefold orientation exhibits less pronounced twin boundary contrast (marked by short solid lines) and diffraction spots than that of Fig. 1. Notice the nearly spherical shape due to the glass matrix.

which may serve as nuclei of fivefold twinned structures occurring during crystallisation [51].

The second mechanism, successive growth twinning on alternate cozoal twin planes, has been observed in-situ during the growth of Au particles on MgO [52] and ex-situ during the growth of Au particles on AgBr [11]. It has been found to be active also in the solid phase crystallisation of amorphous Ge thin films [53] and Si nanoparticles [21]. This mechanism may be illustrated by the HREM image and corresponding structural scheme of Fig. 4 focussing on the characteristic transformation of a threefold twin junction to a fivefold one observed in Ge thin films. In agreement with experimental findings the latter route of twin growth is favoured because of energetic reasons.

The third mechanism, deformation twinning, solely has been observed in thin films up to now, but not in small particles. Thin films deposited on a substrate frequently suffer plane strain deformations arising during crystallisation. Strain relaxation by the introduction of microtwins [54,55] may result in the intersection of twins. This process starts with partial dislocations passing through

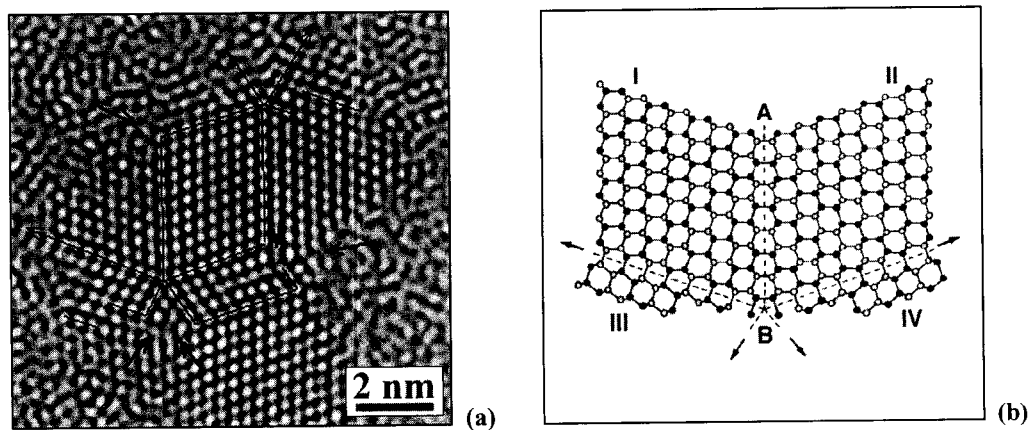


Fig. 4: Multiply twinned particle of Ge grown by solid phase crystallisation of amorphous Ge (a) with twin boundaries marked by thin lines (thick arrows point to higher order lattice defects). The atomic model (b) of the central fivefold axis region represents a situation before by further growth of subunits (III) and (IV) the threefold twin junction at (B) transforms to a fivefold one.

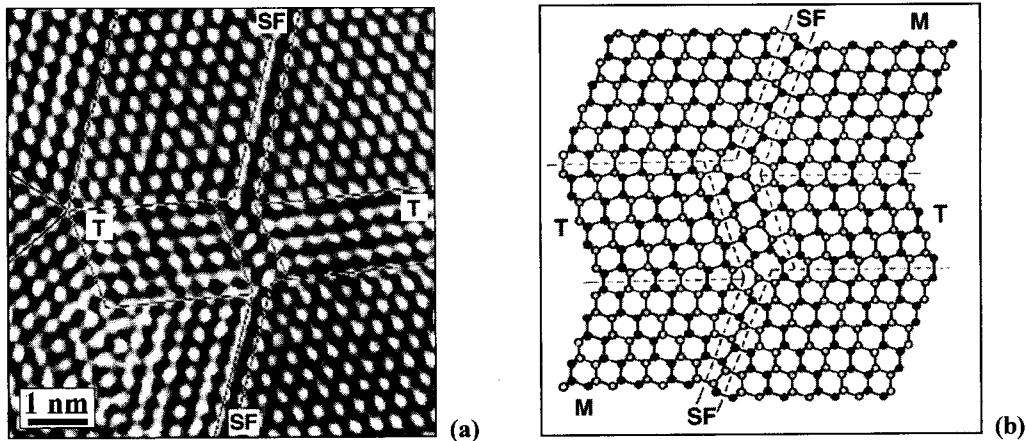


Fig. 5: Twin intersection in a severely twinned particle of Ge grown by solid phase crystallisation (a) and corresponding atomic model (b). The stacking fault (SF) passing through the matrix (M) penetrates a twin band (T) thereby being transformed from an intrinsic to an extrinsic one inside (T) so to form the nucleus of a secondary twin the obtuse angle corners of which are threefold twin junctions.

the strained lattice [56,57] the continuation of which on alternate twin planes consequently will lead to the crossing of twins. A simple case of twin intersection, i.e. penetration of a stacking fault through a twin is represented by the HREM image and atomic model in Fig. 5 (solid phase crystallisation of Ge thin films [53]). The ability of fivefold twinned structures to accommodate large interfacial strains due to lattice misfit and expansivity differences is known from the heteroepitaxial growth of semiconductors on insulating substrates (see, e.g., [35]).

5. Stability and lattice defects

The stability of fivefold twinned structures is an intriguing issue mainly because of the discrepancy between non-crystallographic packing of atoms and its extension in three-dimensional space. MTP's formed from regular fcc or dc crystal units contain spatial discontinuities, thereby introducing inhomogeneous strains. The additional strain and twin energy associated with the formation of MTP's may be balanced by a reduction of surface energy up to a certain size above which transformation to single crystalline particles of cuboctahedral shape should occur. Strain relief by structural modifications (homogeneous lattice distortions) or the introduction of lattice defects (inhomogeneous lattice distortions) may help to extend the range of stability. Related studies are directed to *i.* establish size dependent criteria of stability based on the characteristics of MTP's and their structural fluctuations, *ii.* explain the structural modifications including lattice defects observed in fivefold twinned structures, and *iii.* elucidate size extrema and kinetic transformation barriers.

Energy balance considerations including cohesive, surface, adhesive (particle/substrate), elastic strain and twin boundary energy aimed at calculation of stable size regions for MTP's of transition metals in comparison to their single crystalline counterparts [58-60] provide size limits of , e.g., 27.4 and 273 nm for icosahedral and decahedral MTP's of Ag, respectively. They are, however, of less importance in view of the rapid structural fluctuations observed by real-time video recording in very small metal particles during electron microscopy investigation [61-63]. From the latter studies it was concluded [41] that small particles not necessarily have a single stable structure, but can exhibit a multitude of configurations according to local minima in potential energy. This configurational instability may be understood in terms of statistical fluctuations with the probability of a

particular configuration depending on size and temperature [41].

Experimental observations of fivefold twinned structures give evidence of their extension to sizes far above the size limits calculated by stability considerations. Actually, they are highly distorted and defective in most cases. To account for the absence of observable discontinuities in small sized ($d \leq 12$ nm) transition metal MTP's, according to the model of BAGLEY [64] decahedra may be treated as made up of units with body centred orthorhombic point group symmetry and, analogously, according to the model of MACKAY [65] icosahedra may be treated as made up of units with rhombohedral point group symmetry [66]. Both are only slightly deviating from the fcc structure. By means of such homogeneous lattice distortions always an angle of 72° enclosed by the twin planes is achieved.

At particle sizes distinctly above 10 nm inhomogeneous elastic strains allow rather large reductions of the stored strain energy from which the possibility arises that stress relief processes may occur which involve the formation of lattice defects [60]. Typically, planar defects such as stacking faults and secondary twin boundaries associated with strain field induced dislocation processes are observed [9,20,41]. A particular stress-relieving defect configuration observed in fivefold twinned structures of Si and Ge [18,20,53] consists of regular arrays of tetrahedrally arranged stacking faults meeting at stair-rod dislocations. Such defects lead to an angular lattice dilatation in one of the twin subunits while the neighbouring subunits remain undistorted.

6. Summary

Experimentally observed fivefold twinned structures not only exceed the size limits based on thermodynamic considerations frequently, but also their number density does not distinctly decrease below that of single crystalline particles with increasing particle size [10-12]. These findings rule out that MTP's as whole are frozen in a kinetically metastable state. There are many impressive examples of extremely large sized fivefold twinned structures of various materials which, however, mainly concern decahedral configurations. There are only a few observation of very large icosahedral particles and non of them exceeds the micrometer scale. Obviously, MTP's stabilised by appropriate defect configurations can attain sizes of several hundred nm and larger unless the equilateral growth is disturbed by coalescence and/or transformation phenomena. Despite finally being unfavourably because of energetic reasons, a kinetic barrier prevents the transformation to less defective and non-twinned structures which require more energy than available during the low temperature growth processes concerned.

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