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Condensation, crystallization and coalescence of amorphous Al_2O_3 nanoparticles

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Abstract

The amorphous aluminum oxide (Al_2O_3) nanocondensates produced by energetic pulse laser ablation on Al target under oxygen background gas, for a very rapid heating/cooling effect, have been observed by transmission electron microscopy (TEM). They were found to transform into γ-Al_2O_3 core and amorphous shell in tensile state at a critical diameter of about 20 nm upon electron irradiation. The partially crystallized nanoparticles were unified or twinned over the {1 1 1} plane of the core. This can be rationalized by {1 1 1}-specific coalescence and Brownian rotation of the impinged nanoparticles despite the shell.

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1. Introduction

The interest in aluminum oxide (Al_2O_3) polymorphs stems largely from the use of these materials in a wide range of industries taking advantage of unique bulk and surface electronic structures of the Al–O clusters [1]. Cosmologically, the Al_2O_3 formation via a condensation process is of concern to its natural occurrence in presolar stars [2–4].

Al_2O_3 exists in many metastable polymorphs besides the thermodynamically stable α-Al_2O_3 (corundum form with hcp packing of oxygen) as recently reviewed by Levin and Brandon [5,6]. Among these polymorphs, the spinel-like γ-form with FCC packing of oxygen, finds wide industrial applications as adsorbents, catalysts or catalyst carriers, coatings, and soft abrasives because of their fine particle size and catalytic activity of the surfaces. The γ-Al_2O_3 occurs in nanosize regime (<7.5 nm) [7] due to its lower surface energy yet higher entropy than α-Al_2O_3 [8]. Amorphous Al_2O_3, having four-oxygen coordinated Al ion similar to the case of γ-Al_2O_3 [9], can be formed when the cooling rates approach 10^5 K/s [10] typically for small particles. However, the underlying mechanisms, in particular the critical size and site of nucleation and the coalescence of the impinged nanoparticles, are not clear.

This work intended to clarify these points, using laser ablation condensation technique to synthesize Al_2O_3 nanoparticles originally in the form of amorphous state. Such condensates beyond a certain critical size were found to partially crystallize as γ-Al_2O_3 core and amorphous shell more or less coalesced as single crystal or twin, upon electron irradiation. The thermodynamics and kinetics reasons for the observed phase behavior are also addressed.

2. Experimental procedure

The Al target with negligible impurities (99.9% pure) was subject to energetic Nd-YAG-laser (Lotis, 1064 nm in wavelength, beam mode: TEM00) pulse irradiation. Oxygen gas (99.999% purity) was supplied to oxidize and cool the condensates inside the ablation chamber. Silica glass substrate

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was used to collect the condensates by consecutive laser ablation at 1100 mJ/pulse, 10 Hz and pulse time duration of 240 μs, i.e., power density of 1.5×10^8 W/cm^2 when focused to a beam size of 0.03 mm^2, under oxygen flow rate of 30 and 50 l/min for a total of 30 min. The condensates retrieved from the glass substrate and dispersed in alcohol were dipped onto copper grids overlaid with a carbon-coated collodion film for analytical electron microscopic (AEM) study using JEOL 3010 instrument at 300 keV.

The structures of Al_2O_3 condensates were identified by selected area electron diffraction (SAED), and point-count energy dispersive X-ray (EDX) analysis at a beam size of 10 nm. Bright field images (BFI) taken by transmission electron microscopy (TEM) were used to study the size, morphology and coalescence of the partially crystallized particles. Lattice imaging coupled with two-dimensional Fourier transform and inverse transform was used to study crystallization/vitrification process and to characterize the $\{h\,k\,l\}$-specific coalescence of the γ-Al_2O_3 condensates upon electron irradiation. The d-spacings measured from SAED patterns were used for least-squares refinement of the lattice parameters.

3. Results

3.1. As-condensed amorphous condensates

TEM BFI (Fig. 1a) indicates the as-condensed Al_2O_3 particles are about 10–40 nm in diameter, regardless of oxygen flow rate. These particles are predominantly amorphous, causing diffuse diffraction in SAED pattern (Fig. 1b). There are, however, weak ring diffractions, indicating slight crystallization as γ-Al_2O_3.

3.2. Electron irradiation-induced crystallization and coalescence

Upon electron irradiation at 300 kV for minutes, the amorphous-Al_2O_3 condensates were extensively coalesced and crystallized as γ-Al_2O_3 having Bragg diffraction contrast in BFI (Fig. 2a) and characteristic ring diffractions in SAED pattern (Fig. 2b). Additional observation indicated that amorphous-Al_2O_3 particles became phase separated as γ-Al_2O_3 core and amorphous rim upon electron dosage for about 150 s (Appendix A). Lattice image further shows the crystalline core in drastic contrast to the amorphous shell (Fig. 3a). The nano-size core is nearly spherical and defect free as indicated by two-dimensional Fourier transform (Fig. 3b) and inverse transform in [0 $\bar{1}$ 1] zone axis (Fig. 3c).

The partially crystallized nanoparticles with better-developed planar surfaces tended to coalesce over specific {1 1 1} surface of the γ-Al_2O_3 cores leaving the intruded amorphous shell unsealed as indicated by lattice image in Fig. 4a. Two-dimensional Fourier transform (Fig. 4b) and inverse transform in [0 $\bar{1}$ 1] zone axis (Fig. 4c) further showed the edge-on (1 1 1) twin plane is in fact coherent with respect to the resolved lattice planes. Occasionally, twinning coalesced γ-Al_2O_3 cores were found to have a complete rim of amorphous shell (Fig. 5), presumably due to a better sealing effect.

3.3. Critical size of crystallization

In additional experiment, the amorphous Al_2O_3 condensates dispersed in alcohol were carefully dipped onto a carbon-coated collodion film to exhibit a graded size distribution. This sample was used to study the critical size of crystallization upon electron irradiation. The condensates larger than ca. 20 nm in diameter turned out to crystallize as γ-Al_2O_3 upon electron irradiation for minutes (Fig. 6a). This conclusion was based on the observations of crystalline γ-Al_2O_3 with characteristic Bragg diffraction contrast in BFI (Fig. 6a, Appendix A(b)) and lattice image of the individual particles as mentioned. EDX spectrum

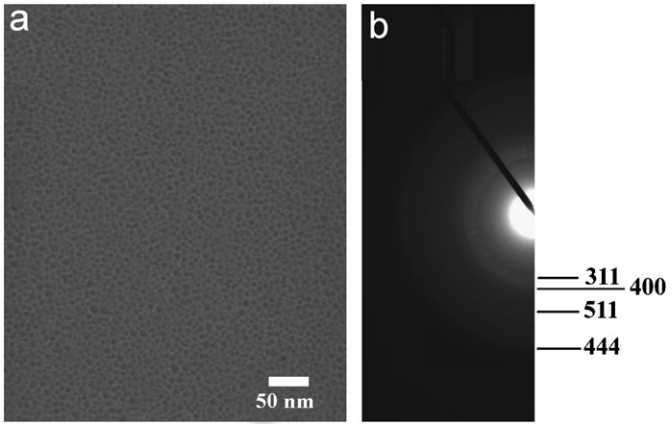

Fig. 1. TEM (a) BFI and (b) SAED pattern of as-condensed amorphous-Al_2O_3 condensates slightly crystallized as γ-Al_2O_3 of minute size as indicated by weak ring-diffractions. Sample produced by laser ablation at 1100 mJ/pulse and oxygen flow rate of 50 l/min.

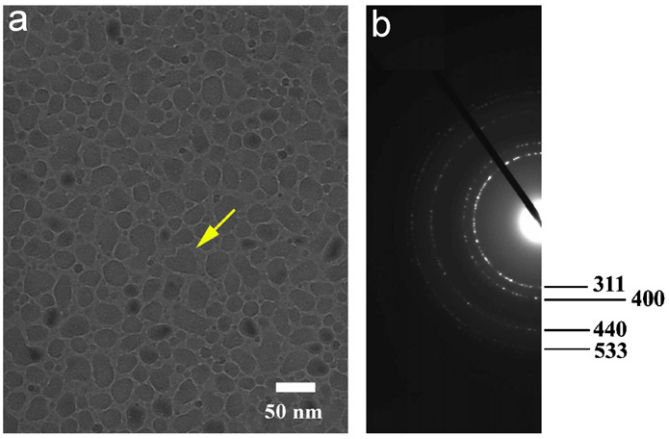

Fig. 2. TEM (a) BFI and (b) SAED pattern showing the Al_2O_3 condensates were more or less coalesced (denoted by arrow) and significantly crystallized as γ-Al_2O_3 with sharp diffractions labeled, when the sample of Fig. 1 was subject to electron irradiation at 300 kV for minutes.