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α- to γ-Al_2O_3 martensitic transformation induced by pulsed laser irradiation

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Abstract

A martensitic transformation from the α to the γ phase of aluminum oxide was observed by transmission electron microscopy (TEM) upon rapid heating induced by pulsed laser irradiation. Two variants possessing a twin relationship were found in the product. High-resolution TEM reveals that the transformation is achieved via the glide of quarter partial dislocations on every other basal plane of α-Al_2O_3. The high thermal stress caused by pulsed laser irradiation is believed to be the main driving force of the phase transformation. This martensitic transformation is associated with a positive volume change and substantial shear strain. The overall shear strain could be minimized by the self-accommodating variants. These characteristics suggest potential application of the martensitic transformation for transformation toughening in ceramic materials.

Keywords: Martensitic phase transformation; Ceramics; High-resolution electron microscopy; Twinning; Alumina

1. Introduction

Aluminum oxides exist in many different forms, namely α, β, γ, η, θ, κ and χ phases. Except for the stable phase α-Al_2O_3, the other phases are termed transition alumina, obtained during the calcination of aluminum hydroxides [1–3]. Due to its application as a catalyst and catalytic support, γ-Al_2O_3 is the most prominent transition phase. Thus, γ-Al_2O_3, as well as the phase transition from γ- to α-Al_2O_3, has been extensively studied [4–8]. Raising the temperature above a critical level induces a gradual transformation of γ-Al_2O_3 to α-Al_2O_3 by a diffusion-controlled nucleation and growth process. However, the reverse transformation from α- to γ-Al_2O_3 does not occur on cooling. With strong laser irradiation or ion beam bombardment α-Al_2O_3 can be transformed to γ-Al_2O_3 [9–11]. However, these transitions involve either liquid or amorphous aluminum oxides as intermediate phases. Up to now, to our knowledge, direct transformation from stable α-Al_2O_3 to metastable γ-Al_2O_3 has not yet been achieved, on either heating and cooling. In this work we report a martensitic transformation from α- to γ-Al_2O_3 induced by pulsed laser irradiation.

Martensitic transformation has been known for more than a century, starting with quenched steels. Since then it has been found in many other metals, alloys and ceramics. This transformation is related to many remarkable properties, such as the shape memory effect, transformation induced plasticity and transformation toughening [12–16]. Whilst the investigation of martensitic transformations has made great progress in recent decades, the nucleation and growth mechanisms of martensite are not yet fully understood. Generally, defects in the parent phases are believed to assist the nucleation of a martensitic embryo, while the growth of martensite is accomplished by motion of the phase interface, which involves atomic shuffling and/or dislocation motion. For the fcc to hcp transformation Olson and Cohen

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[17] suggested a stacking fault model for martensite nucleation, while the growth of martensite could be realized by Shockley partial dislocations gliding on alternate (1 1 1) planes. This mechanism has been clearly demonstrated in experiments on a Co–Ni alloy [18]. In our work the reverse process to this mechanism, i.e. transition from an hcp to a fcc lattice, has been explored to interpret the martensitic transformation from α- to γ-Al_2O_3. Based on our transmission electron microscopy (TEM) observations and the interfacial dislocation model [19] the transformation mechanism is proposed to be gliding of partial dislocations on alternate (0 0 0 1) planes of α-Al_2O_3. A probable nucleation mechanism is suggested for the partial dislocations. The driving force of this martensitic transformation is attributed to the high thermal stress induced by rapid heating. Additionally, the martensitic transformation from α- to γ-Al_2O_3 features a positive volume change, a relatively large shear component of shape strain and twinning formation. As a result, this system could be a potential means of transformation toughening ceramic materials.

2. Experimental methods

The material we used for this study was commercially available GaN/sapphire (α-Al_2O_3) films grown by molecular organic chemical vapor deposition (MOCVD). The thickness of the GaN layer was about 7 μm and that of the sapphire substrate was about 455 μm. The pulsed laser irradiation of α-Al_2O_3 was conducted by laser lift-off (LLO) processing [20], which is widely used in separating GaN epitaxial films from an α-Al_2O_3 substrate. In the LLO process the sapphire substrate is transparent to a pulsed laser beam of specified frequency, however, the laser beam is absorbed by the GaN material. During treatment the GaN side of the GaN/sapphire sample was bonded to a quartz crystal for support and the laser pulsing was conducted from the sapphire side. Thus, the photon energy was transformed to thermal energy at the GaN/sapphire interface, rapidly heating the interfacial area and causing decomposition of the interfacial GaN into gaseous nitrogen and metal droplets. Consequently, the epitaxial film can be separated from the sapphire substrate. In this work the laser had a wavelength of 248 nm, an energy density of 0.5 J cm^{-2}, a beam diameter of 1.5 mm and a pulse duration of 20 ns, with only one pulse applied. After the LLO treatment cross-sectional specimens of the thin film were prepared by polishing, dimpling and ion milling. TEM and high-resolution TEM (HRTEM) investigations were performed on a Tecnai F30 microscope (FEI Co., Eindhoven, The Netherlands) operating at 300 keV.

3. Results

3.1. Optical microscopy observation

After pulsed laser irradiation the GaN film was separated from the sapphire substrate. The exposed surface of the sapphire substrate was mirror-like and smooth, with no defects or features visible under optical microscopy (Fig. 1), although a few metal droplets could be found on the surface. In contrast, the exposed surface of the GaN film was visibly rough, but with no cracks found at the surface. This suggests that most of the laser energy was absorbed by the GaN and separation of the thin film was caused by decomposition of the interfacial GaN layer into liquid Ga and nitrogen gas.

3.2. The phase transition layer

TEM investigations revealed that after LLO processing the layer of α-Al_2O_3 had been transformed to γ-Al_2O_3 at the GaN/sapphire interface, with a transition layer thickness of about 100 nm (as shown in Fig. 2a). Electron diffraction patterns of the transformed γ-Al_2O_3 are shown in Fig. 2b and c. The interface between the transformed γ- and α-Al_2O_3 was macroscopically straight and largely parallel to the (0 0 0 1) plane of the α-Al_2O_3. Below the phase interface, dislocations and stacking faults were observed (as indicated by the white arrow in Fig. 2a). The orientational relationship between the γ-Al_2O_3 layer and α-Al_2O_3 substrate was determined to be $(1\,1\,1)_\gamma//(0\,0\,0\,1)_\alpha$, $[1\,1\,2]_\gamma//[1\,1\,-2\,0]_\alpha$ and $[1\,1\,0]_\gamma//[1\,-1\,0\,0]_\alpha$ by electron diffraction nd HRTEM observation. By comparing the

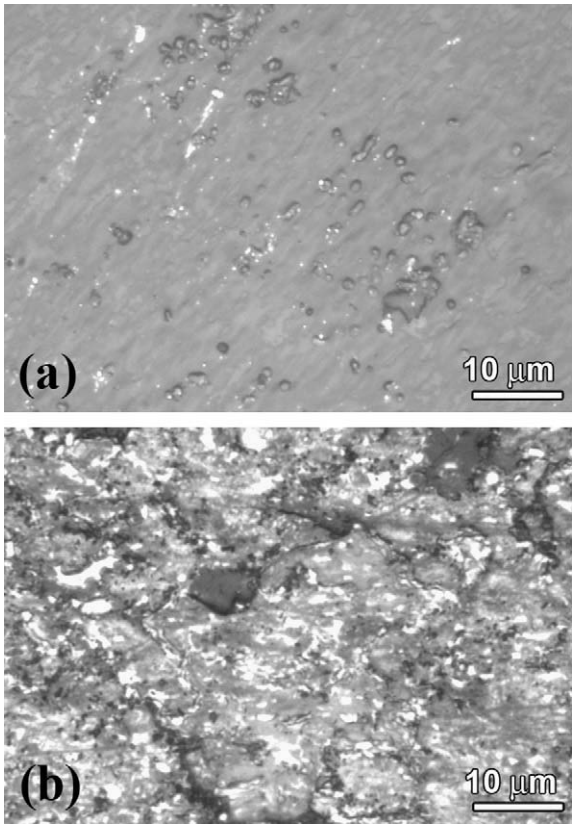

Fig. 1. Optical micrographs of the exposed surfaces of (a) the sapphire substrate and (b) the GaN film after the process. The exposed GaN surface is visibly rougher than the exposed sapphire surface.