

Formation of Strontium Titanate Bicrystal by the Spark Plasma Sintering Method

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Spark plasma sintering (SPS) is a technique used for enhanced consolidation of powdered compacts by utilization of pulsed direct current and high uniaxial pressure. Physical mechanisms for densification of these powders as well as subsequent grain growth anomalies are debated in literature [1]. Limited information is available regarding the influence of electric fields on grain boundary formation and resulting core structures [2]. Bicrystals, created by manipulation of two single crystals to form a grain boundary with selected orientation, are the ideal method for study of fundamental grain boundary structures as a function of processing effects [3]. Forming bicrystals via parameters used in SPS provides an avenue to determine the impact of electric fields on grain boundary formation. In this study, strontium titanate (SrTiO_3) bicrystals were successfully formed, for the first time, at high pressure with moderate temperatures and times by SPS apparatus. Scanning electron microscopy (SEM) determined the quality of the interface bonding. Transmission electron microscopy (TEM) techniques combined with spatially resolved electron energy-loss spectroscopy (EELS) showed atomically resolved grain boundaries with no secondary phases.

Two single (100) SrTiO_3 crystals were fixed with a nominal misorientation of 0° , 4° , or 45° around $\langle 100 \rangle$ axis and then positioned within a SPS apparatus (Fig. 1). Bonding temperatures and times were systematically altered to maximize quality of the bonded interface. Uniaxial pressure of 120-140MPa was applied to minimize contact resistance. A 12-2 DC pulse sequence was used with a pulsed bias of 4V and direct current of 550A. Fraction of interface bonding was characterized via SEM. Bicrystals with a 0° twist orientation had a bonded interface greater than 95% at temperatures of 600°C and 700°C for a bonding time of 90 minutes. A 4° twist angle bicrystal was formed at a temperature of 800°C for 20 minutes with a bonded interface of 70%. Lastly, a 45° twist angle bicrystal was formed at a temperature of 800°C for 90min with a bonded interface of 45%. Bonding parameters were altered for 4° and 45° twist orientation to increase interface bonding. High angle misorientation boundaries have a large structural mismatch between the two half-crystals, which leads to higher interfacial stress states during bicrystal formation and hinders cross-boundary diffusion. A focused ion beam instrument was used to prepare cross-sectional TEM samples for high-angle annular dark field (HAADF) imaging by scanning TEM (STEM). HAADF-STEM images of the 4° twist bicrystal show an atomically ordered boundary with periodic distortions (Fig. 2). These distortions appear similar to screw dislocations found at the boundary of low angle twist SrTiO_3 bicrystals by Fitting *et al* [4]. HAADF-STEM images of the 45° twist bicrystal show an atomically ordered boundary with no secondary phases or amorphous films (Fig. 3). Spatially resolved EELS across the boundary coincides with EELS data from SrTiO_3 bicrystals with twist boundaries formed by conventional methods [4]. Thus, the first successful formation of SrTiO_3 bicrystals by SPS apparatus is reported. Future work will be focused on forming bicrystals by SPS technique to systematically study the effect of electric fields and heating rates on specific grain boundary structures. [4]

References:

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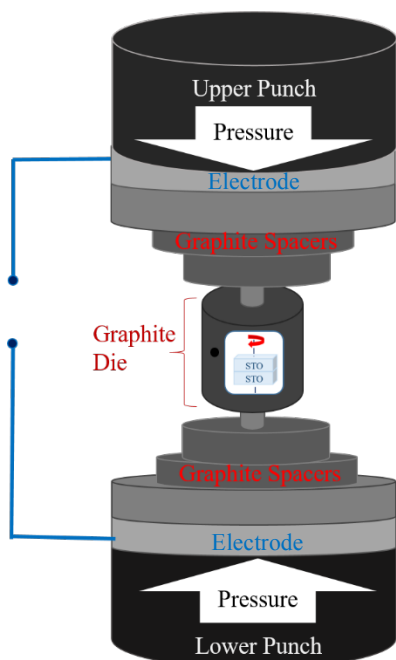


Figure 1: Schematic of experimental setup for SrTiO₃ bicrystal formation by SPS apparatus

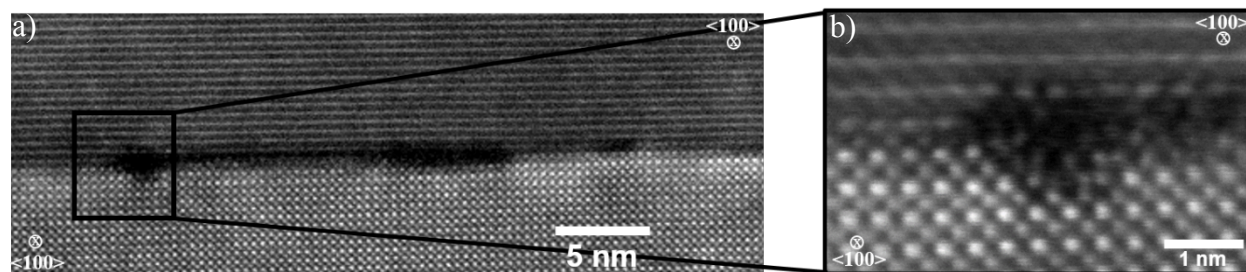


Figure 2: (a) and (b) HAADF-STEM images of boundary with nominal 4° misorientation, recorded in <100> zone axis. Bicrystal formed at 800°C for 20 minutes.

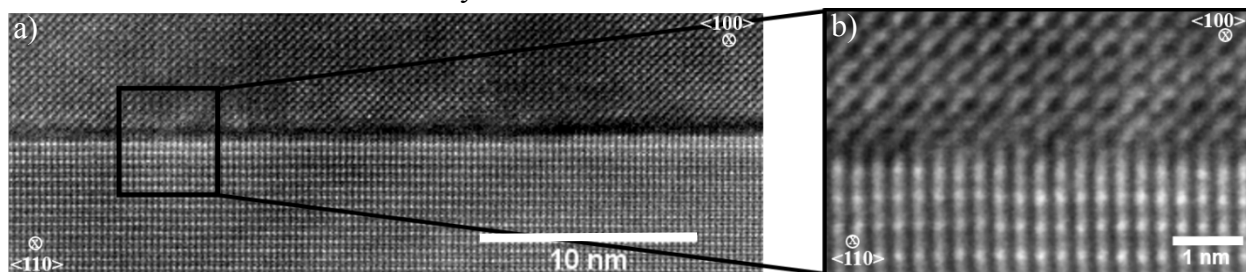


Figure 3: (a) and (b) HAADF-STEM images of boundary with nominal 45° misorientation, recorded in <110> zone axis. Bicrystal formed at 800°C for 90 minutes.