Structural Analysis of Cr-rich Luminescent Phase Formed along an Alumina Grain Boundary

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The optical properties of ruby (Cr-doped sapphire) have been extensively studied so far because of the importance as the firstly discovered laser material. By recent studies, it has been shown that when alumina nanostructures, such as thin films, nanowires and nanobelts, contain Cr^{3+}, they exhibit luminescent properties. For instance, N. Yu et al. reported the fabrication of ruby thin films on surfaces of α-Al_2O_3 substrates and their luminescent properties [1]. However, the methodology for forming a ruby thin phase inside the bulk crystal has not been established.

In this study, an alumina bicrystal with a Cr-doped $\{1\bar{1}00\}/[0001]$ 2° low-angle tilt grain boundary was fabricated by diffusion bonding at elevated temperatures. The detailed bonding condition can be found in our previous papers [2]. The samples for Transmission electron microscopy (TEM) observation/analysis were prepared by standard procedures using ion milling method. These samples were observed by conventional TEM (JEOL JEM-2010HC, operated at 200 kV) and high resolution TEM (HRTEM; JEOL JEM-4010, operated at 400 kV). The composition around the grain boundary was analyzed using TEM-Energy dispersive X-ray spectroscopy (EDS) (Topcon EM-002BF, operated at 200 kV) with the probe size of approximately 1.5 nm. The luminescent properties of the grain boundary were examined using confocal micro-luminescence spectroscopy (TOKYO INSTRUMENTS, model NanoFinder30) with high spatial resolution (1 μm). Here, a Nd: YAG laser with a wavelength of 532 nm was used as the excitation light.

A low-magnification bright-field TEM image of the grain boundary is shown in FIG. 1. It can be seen that the crystals are bonded with a secondary phase in between. The thickness of the secondary phase is estimated to be about 200 nm. In order to investigate the composition around the secondary phase, TEM-EDS point analysis was conducted. Typical spectra obtained from an area inside the secondary phase and an area approximately 3 nm outside the phase are shown in FIG. 2(a) and (b), respectively. Cr-induced peaks can be obviously seen in the spectrum (a), but not in the spectrum (b). Thus, it can be concluded that the secondary phase is enriched with Cr atoms.

To investigate the luminescent property of the Cr-rich secondary phase, the confocal micro-luminescence spectroscopy was performed at room temperature in air. Figure. 3 shows an intensity map of the ruby induced luminescence at 694.2 nm. The distribution of the luminescence was detected along the grain boundary. Hence, it can be said that we managed to fabricate a Cr^{3+}-rich luminescent phase along a grain boundary of alumina.

It is also noticed from the FIG. 1 that a wavy array of dislocations is formed at the center of the secondary phase. This is the array of low-angle grain boundary dislocations introduced due to compensate for the mistilt angle of the boundary. Also, we can see other dark contrasts in between the alumina matrix and the Cr-rich secondary phase. These contrasts are originated from the misfit dislocations which are introduced to compensate slight lattice mismatches between the matrix and the secondary phase. To confirm the misfit dislocation structures, TEM observation was conducted from the $\langle 1\bar{1}00 \rangle$ plan-view direction. Figure. 4 shows a bright-field TEM image of the interface. The formation of very complex misfit dislocation network structures can be seen. Besides, misfit dislocations were found to dissociate into partial dislocations with 12 to 16 nm intervals. From crystallographic point of view, stacking faults must be introduced in between these dissociated dislocations. Here, the measured stacking fault width was rather wide compared to the stacking fault width formed in alumina $\{1\bar{1}00\}$ planes reported so far [3]. These results suggest that the stacking fault energy of the interface may be significantly lowered by the presence of Cr ions.

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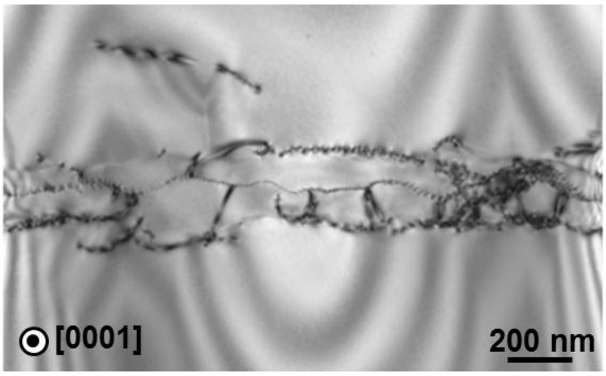

FIG. 1. A BF-TEM image of the grain boundary observed from [0001] direction. The formation of an approximately 200 nm width secondary phase can be seen.

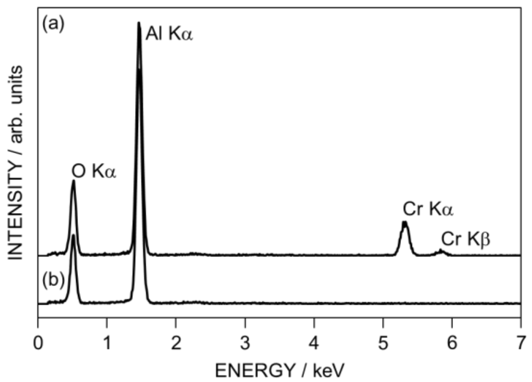

FIG. 2. TEM-EDS spectra obtained (a) at an area in the secondary phase and (b) at an area 3 nm outside the secondary phase-alumina matrix interface.

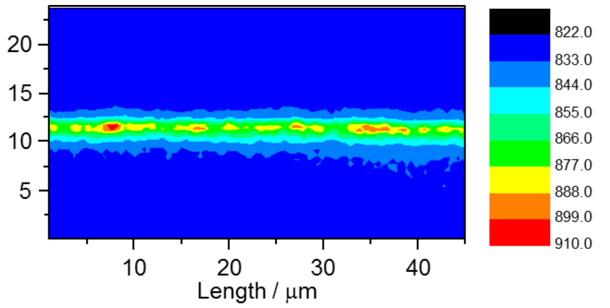

FIG. 3. Intensity map of the ruby induced luminescence at 694.2 nm obtained by using confocal micro-luminescence spectroscopy. The distribution of the luminescence was detected along the grain boundary.

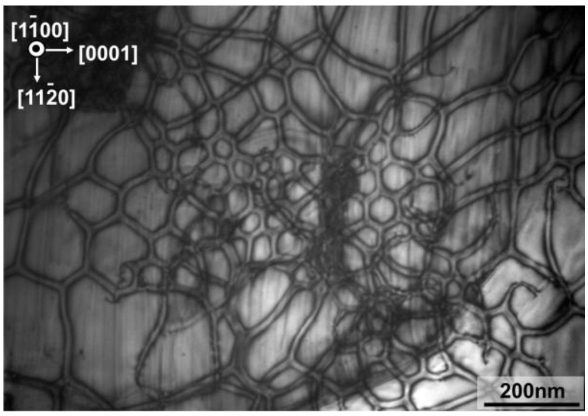

FIG. 4. A BF-TEM image of the secondary phase-alumina matrix interface observed from [1$\bar{1}$00] plan-view direction. The formation of a complex misfit dislocation network structure was observed.