

ORIGIN OF IMPERFECTIONS IN $\langle 100 \rangle$ SrLaAlO₄ CRYSTALS

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In Czochralski-grown SrLaAlO₄ crystals with $\langle 100 \rangle$ orientation, (001) planar faults extending through the entire crystal boule can frequently be observed. Chemical etching and transmission electron microscopy including energy dispersive X-ray spectroscopy were used to characterise their nucleation sites, these being located in the upper part of the crystal cone. Three serious sources were found: (1) lateral {001} facets, (2) grown-in defects in the seed, and (3) small particles of a second phase in the interior of the cone. These particles were identified as trigonal and cubic form of lanthanum oxide with a different Sr content.

PACS numbers: 61.72.Ff, 81.65.Cf, 81.30.Mn

1. Introduction

SrLaAlO₄ (SLA), which belongs to the oxides that crystallise in the tetragonal [K₂NiF₄] structure, has attracted attention for its use as a substrate in the epitaxial growth of high- T_c superconducting films such as Y-Ba-Cu-O [1-4], Bi-Sr-Ca-Cu-O [2], and La-Sr-Cu-O [5]. For application, substrate crystals with good crystallographic perfection are favourable. Twinning is not a problem during the growth of SLA crystals. However, narrowly spaced (001) planar defects extending through the entire crystal boule are frequently observed (Fig. 1). Recent transmission electron microscope (TEM) studies revealed that this stacking disorder consists of differing compositional (chemical) faults [6]. Optical examination indicates that the faults are very probably generated during the initial stage of the growth process (i.e. during seeding and shouldering). Therefore their origins must be located in the crystal cone near or on the seed. In order to characterise the nucleation sites, chemical etching and TEM investigations were performed in this area.

2. Experimental procedure

SLA crystals were grown by the Czochralski method using an automated pulling device with RF induction heating. An active bottomheater and afterheater allowed the temperature gradients to be adjusted. The crystals were grown in a

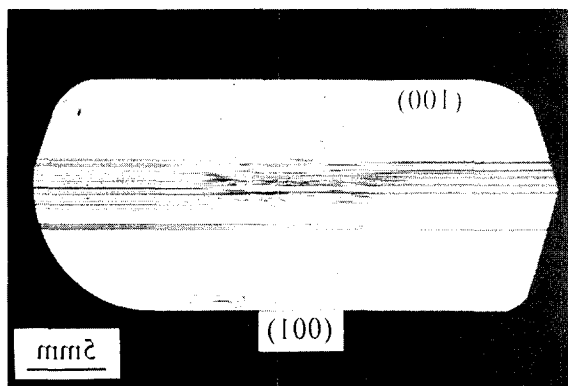


Fig. 1. (100) cross-section of a SLA crystal showing typical planar faults, made visible using the schlieren technique. The defect lamellae are aligned with the lateral {001} faces.

pure nitrogen atmosphere at a pulling rate as low as 1.5 mm h^{-1} and a rotation rate in the range of 10 to 30 rpm. To achieve a stable solid/liquid interface, the (100) seed orientation was chosen. Consequently the growth took place mainly on {110} facets [7].

To examine the beginning of the growth process, lateral {010} faces (i.e. parallel to the growth direction) were prepared at the crystal cone, including the adjacent section of the seed, by lapping and polishing. The specimens were subsequently chemically etched to reveal crystallographic defects. An overall view of the defect's configuration was obtained by repeating this procedure several times, progressing from the periphery to the centre of the cone. For etching, a dilute 2% HCl was used at 40°C [8]; the etching time was in the range of 2 to 10 min.

Foils for TEM examination were prepared from regions containing a high defect density according to standard techniques (drilling, grinding, final thinning by ion beam milling). Conventional TEM in the diffraction contrast mode was carried out at a 1000 kV accelerating voltage. Analytical TEM was performed using a HITACHI H-8110 microscope, equipped with a KEVEX energy dispersive X-ray spectrometer.

3. Results and discussion

Figure 2 demonstrates a typical defect distribution at the top of a cone and the adjacent part of the seed. Frequently, a thin section with a low defect level separates the cone from the seed (arrows). There are etch pits (microdefects) inside the seed; traces of planar defects were not observed (cf. Fig. 2, region 1). The interior of the crystal cone is characterised by some heavily disturbed zones (e.g. region 2), which obviously induce extended (001) planar defects. A very high defect content appears in the lateral {001} zone (shouldering; region 3), however long-range planar faults do not originate.

The sites for formation of (001) planar faults during the initial stage of crystal growth are illustrated in detail (cf. Fig. 3):

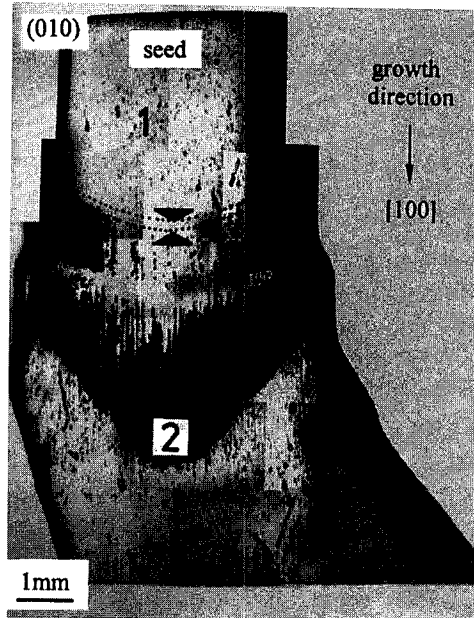


Fig. 2. Defect distribution on the upper part of a crystal cone. The $\{010\}$ surface has an orientation parallel to the growth direction and was prepared from the cone's centre and subsequently chemically etched.

(a) Generally, $\{001\}$ facets exist at the beginning of shouldering. They can cause instabilities of the meniscus (varying meniscus height) that result in rapid crystallization (lateral growth) by increased supercooling and sometimes in the generation of (001) planar defect bands (Fig. 3a).

(b) Small grown-in defects are present inside the seed and can act as nuclei ("dragging" effect) as the example given in Fig. 3b. There are some traces of (001) planar faults that originate from etch pits on the seed and spread into the cone.

(c) The heavily disturbed regions observed in the interior of the cone may be able to induce planar faults. Traces of numerous planar defects that emerge from this area and propagate into the bulk are visible (Fig. 3c).

In order to show the existing sources inside the heavily disturbed regions, chemical etching is unsuitable. Therefore, TEM investigations were performed to clarify their nature. Figure 4a illustrates the very high density of crystallographic defects such as particles, dislocations and narrowly spaced planar defects in this zone, as expected from the etching experiments. The particles can reach lateral dimensions of $1 \mu\text{m}$ and about 100 nm in thickness. They operate as powerful sources for different imperfections, including (001) planar defects. The example, given in Fig. 4b, shows a single extended defect, consisting of a thin plate-shaped particle in its centre, punched partial dislocation loops and an expanded (001) planar fault.

The identification of the particles was carried out by electron diffraction (selected area diffraction, SAD) and energy dispersive X-ray spectroscopy (EDX).

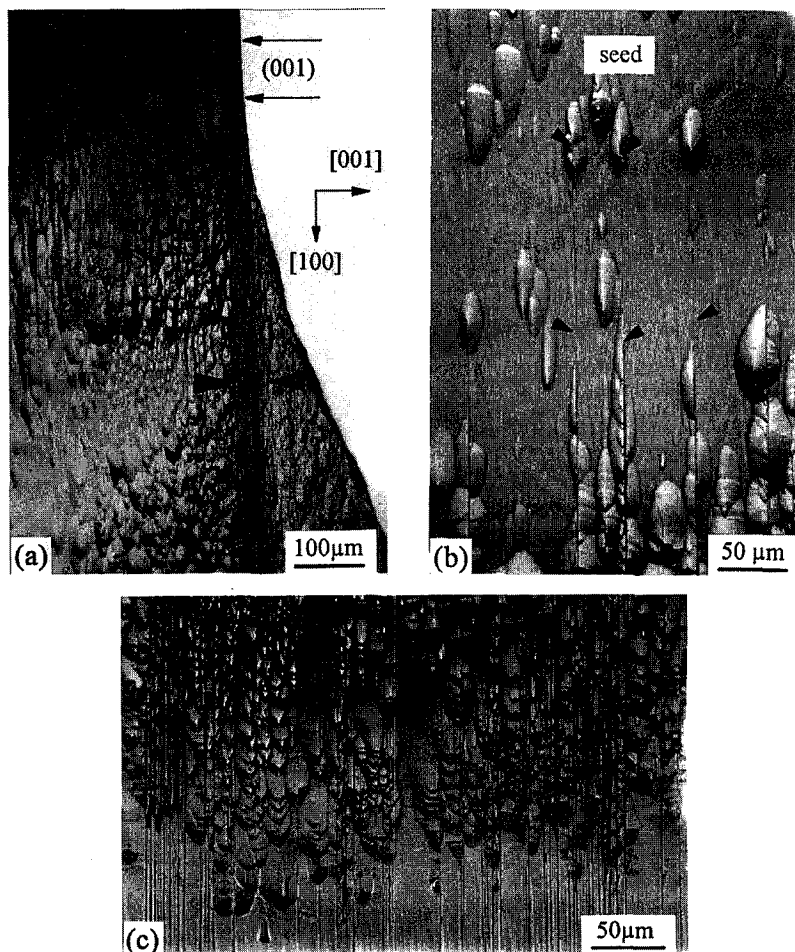


Fig. 3. Creation of planar defects during the initial stage of crystal growth. The chemically etched $\{010\}$ slices stem from different crystal cones. (a) Formation of a large planar defect band on a lateral $\{001\}$ facet at the beginning of shouldering. (b) Transition region between seed (above) and crystal cone (below). The creation of long-range (001) planar faults (arrows) is visible. (c) Detail from the lower part of a heavily disturbed region near the centre of a cone.

Two lanthanum oxide phases, differing in their structure, were identified from the diffraction patterns: (1) the ordinary trigonal *A* phase (space group $P\bar{3}m1$) which is stable at room temperature, and (2) the cubic *X* phase ($Im\bar{3}m$) with a small unit cell (high temperature form). The lattice constant of the *X* form taken from [9] and the measured one are 4.60 \AA and 4.51 \AA , respectively. The difference may be caused by the additional Sr content (cf. Table). This may also stabilise the cubic high temperature phase at room temperature. Although there is commonly a noticeable proportion of Sr, La-Sr-O compounds have not, up till now, been found.

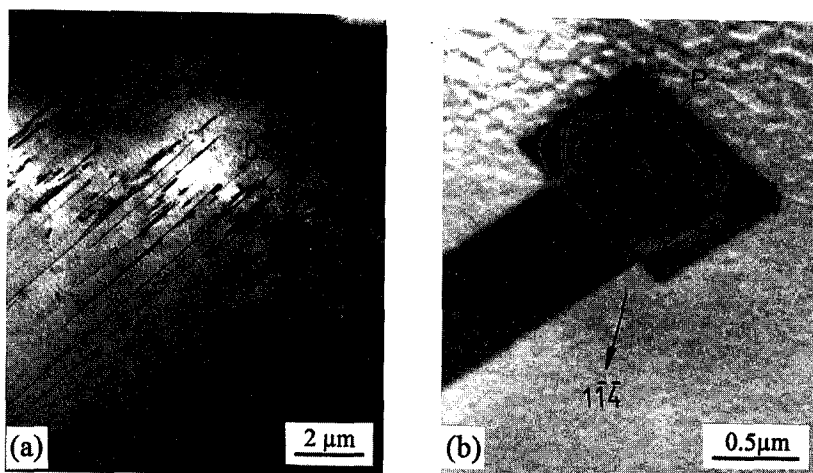


Fig. 4. TEM micrographs of lattice defects, present in specimens obtained from a heavily disturbed region near the cone's centre. (a) Area with a high density of particles, dislocations and narrowly spaced planar defects (in edge-on position). Foil orientation and viewing direction is $[100]$. (b) Single extended defect, consisting of plate-shaped particle in its centre (P), partial dislocation loops and an expanded planar fault (PF). Foil orientation is $[001]$.

TABLE

Mean values of the EDX analyses from the particles (the results are given as ratio of the molecular proportion of Al and Sr to La).

Element	Particles	
	A phase	X phase
Al K	0.06	(0.06)
Sr L	0.07	0.14
La L	1 ^a	1 ^a

^aThe molecular proportion of La was normalised to 1.

4. Summary

The nucleation sites of long-range (001) planar faults in Czochralski-grown $\langle 100 \rangle$ SLA crystals are mainly located in the top of the crystal cone. Three important sources were found: (1) formation at lateral $\{001\}$ facets at the beginning of shouldering, (2) grown-in defects in the seed, which can act as nuclei, and (3) small particles of a second phase, present in the heavily disturbed region around the cone's centre.

Using SAD and EDX, these particles were identified as differing lanthanum oxide phases containing a varying proportion of additional Sr. The presence of

second phase particles suggests that careful choice of the initial melt composition is one important factor in avoiding the generation of (001) planar defects. Further investigations are under way to clarify the mechanism for formation of the planar defects at particles.

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