Functional Materials 11, No.1 (2004)

Formation of the spinel structure ($AlAl_2O_4$) phase on sapphire surface

N.S.Sidelnikova, M.A.Rom, A.Ya.Dan'ko,
S.V.Nizhankovsky, U.V.Sirik, S.I.Krivonogov

Institute for Single Crystals, National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

Received April 2, 2003

A phenomenon of transformation of sapphire surface layer with the formation of a new cubic phase of spinel ($AlAl_2O_4$) structure as a result of high temperature reducing annealing has been revealed. The result of microscopic investigations and X-ray diffraction analysis of the new phase layer on sapphire surface for two crystallographic planes (0001) and ($10\bar{1}2$) are presented.

Обнаружено явление трансформации поверхностного слоя сапфира с образованием новой фазы с кубической структурой шпинели ($AlAl_2O_4$) в результате высокотемпературного восстановительного отжига. Приведены результаты микроскопических исследований и рентгеновского фазового анализа слоя новой фазы на поверхности сапфира для двух кристаллографических плоскостей (0001) и ($10\bar{1}2$).

It has been shown [1] that specific defects (the light scattering centers) are formed under certain conditions in sapphire crystals grown by horizontal directional crystallization method (HDC) in the media contained reducing components (H_2, CO) due to a stoichiometry disturbance of the Al_2O_3 melt. These defects are of 1 to 3–5 μm size and are characterized often by orthogonal (pseudo-cubic) faceting, thus, those can be considered as inclusions of a phase depleted of oxygen (admittedly $AlAl_2O_4$) with the structure different from that of α–Al_2O_3. Today, there are neither direct data on the composition and structure of these defects, nor sufficient information on the formation possibility of the $AlAl_2O_4$ phase at a high degree of Al_2O_3 reduction. The only exception is the work [2] where the investigation results are presented of the reduction products of the high-alumina raw material for electro-corundum by solid carbon. An isotropic phase was discovered in the reduction products having fcc structure of the spinel type with lattice parameter $a = 7.915$ Å; it was identified as $AlAl_2O_4$.

Since it is assumed that that the micro-inclusions formation in sapphire is due to the melt critical supersaturation in oxygen vacancies, it is necessary to determine an opportunity of $AlAl_2O_4$ phase formation during Al_2O_3 reduction with a gaseous reducing agent (CO) without contact with carbon (graphite). Before, it has been established that the micro-inclusions resulting from solid-phase reactions are not formed in crystal even at near-melting temperatures [1]. It has been assumed that at high supersaturation degree in oxygen vacancies, the reaction $3Al_2O_3 + V_o^{2-} \rightarrow 2AlAl_2O_4$ could proceed in a thin surface layer contacting immediately with reducing media. The transformation of this layer has been studied during high temperature annealing in the media having high reducing potential. The results of these investigations are presented in this work.

The previously machined plane-parallel sapphire samples with crystallographic ori-

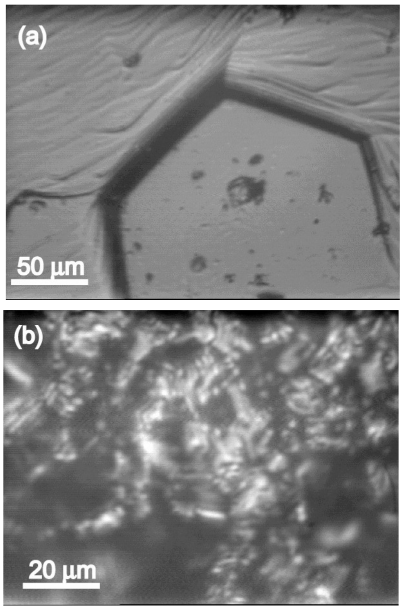

Fig. 1. Transmission microscopic images of the (0001) sapphire surface after high-temperature reducing annealing (~1800°C): (a) etching traces on the sapphire surface; (b) layer with the new phase content of about 97 % (t ~ 2.5 μm).

entation planes (0001) and (10$\bar{1}$2) on the surface were used in the experiments. The experiments were carried out in a furnace with carbon-graphite heat screens [3]. After preliminary vacuum heat treatment at 900°C until the pressure range of <0.1 Torr was attained, the chamber was filled with Ar until the pressure range of the 800 Torr, and samples were heated up to necessary temperature. The sample temperature was controlled by a W + 5 % Re–W + 20 % Re thermocouple, which preliminary was calibrated using reference points. The annealing time was 5 to 10 h. During the annealing, the gaseous media composition (CO and H_2 content) was monitored using a GASOCHROM-3101 gas analyzer. The surface morphology changes after the annealing were investigated using a MIK-4 optical microscope. The X-ray investigations were done using a DRON-1.5 diffractrometer in $CuK\alpha_{1,2}$ radiation (monochromator-(002) pyrocarbon).

It was found that high temperature reducing annealing in certain conditions causes the changes in sapphire surface morphology (Fig. 1,2) that are not typical of the etching [3]. In these cases, a layer was observed on the sapphire surface differing in phase composition. The thickness of polycrystalline zone formed on the sapphire substrate was determined as an approximation of the homogeneous screen attenuating the single crystal reflection [4] as well as from intensity of its inherent interference lines in symmetrical Bragg geometry [5]. As a rule, the t values (effective thickness of the polycrystalline zone) obtained in both geometries were coincident, although it was

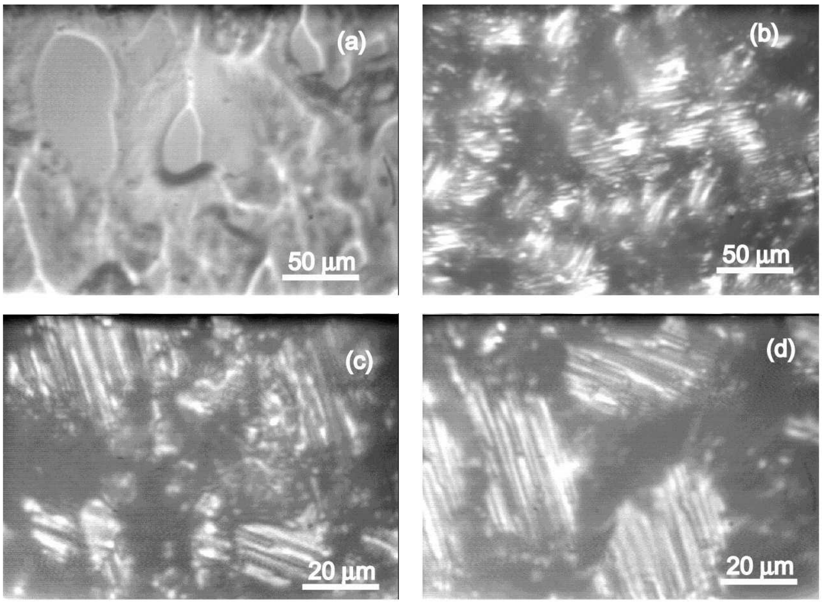

Fig. 2. Transmission microscopic images of the (10$\bar{1}$2) sapphire surface after high temperature (~1800°C) reducing annealing: (a) etching traces on the sapphire boundary surface; (b) the layer having 90 % content of the <311> texture new phase (t ~ 10–30 μm); (c), (d), areas of the (b) layer having strongly pronounced texture.

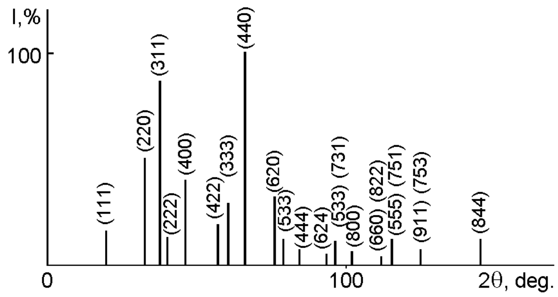

Fig. 3. X-ray diffraction pattern for $AlAl_2O_4$ at the (0001) sapphire substrate, $CuK\alpha_{1,2}$ radiation.

observed non-uniformity of *t* value over the crystal surface area. It has been established that depending of experiment conditions (temperature, the reducing medium composition, surface treatment conditions), the *t* value varies from 2.5 to 40 μm.

X-ray phase analysis of the surface layer was done in θ–2θ geometry. It has been established that polycrystalline phase synthesized on sapphire Al_2O_3 substrate belongs to cubic syngony *Fd3m*. All interference lines of this zone shown in the schematic X-ray diffraction pattern (Fig. 3) correspond to spinel structure with lattice period a_o~7.92 Å. If the intensities of the $AlAl_2O_4$ phase interference lines are close to calculated kinematic values (Fig. 3), then the acute <311> texture is observed on the surface $(10\bar{1}2)$ (Fig.2 b, c, d). The analysis of θ–2θ diffraction patterns allows to determine that the pole density P_{311} is 25 times higher than corresponding values for isotropic polycrystal. The normalization has been carried out by Morris method [6] using thickness *t* of the layer forming the pattern.

The evaluations of gaseous media composition in the experiments (using GAZOHROM-3101 gas analyzer) have shown that the fraction of reductive component ($CO + H_2$) is about 20 %. The corresponding concentration of oxygen vacancies in the boundary Al_2O_3 layer may attain 10^{19} cm^{-3} and higher [7]. Such oxygen loss from Al_2O_3 lattice cannot result in the complete transformation Al_2O_3 layer in $AlAl_2O_4$ layer. However, it can be assumed that the high vacancy concentration causes nucleation of a new phase, which, being crystallized in cubic syngony, may grow in part at the expense of gaseous component (Al, AlO, Al_2O).This assumption is confirmed indirectly by the results of experiments where the sapphire surface was screened in part against the gas influence during annealing. In this case, traces of thermochemical etching were observed in the screened area (Fig. 1a), while new phase layer was formed at the "open" surface (Fig. 1b). In the transition area, objects can be observed changing from etching figures in morphology; perhaps those must be the islands of new phase (Fig. 4).

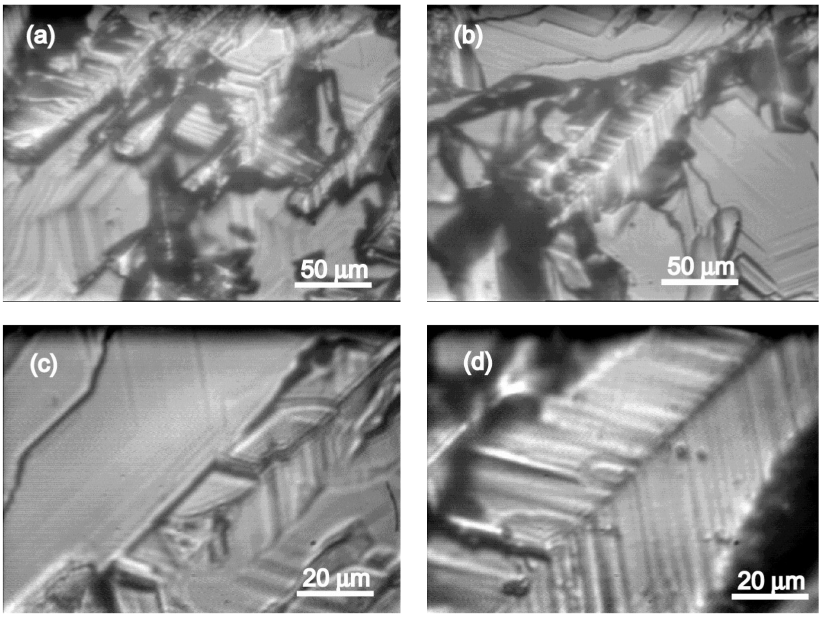

Fig. 4. Transmission microscopic images of the (0001) sapphire surface after high-temperature reducing annealing (~1800°C): (a), (b), (c), (d), different areas of the transition zone from "screened" to "open" area.

Thus, the transformation phenomenon of sapphire surface layer with new phase formation having cubic spinel $AlAl_2O_4$ structures has been revealed as a result of high-temperature reducing annealing. The opportunity of ($AlAl_2O_4$) phase formation under high level of sapphire reducing ($\alpha-Al_2O_3$) proved by experiments witches in favor of the before-mentioned [1] assumptions about formation causes and structure of light scattering centers in sapphire grown in reductive gaseous media. Perhaps the further study of that phenomenon will contribute to complete comprehension of defect formation during crystal growth. In conclusion, it is to note that investigation of the revealed phenomenon as well as the structure and physical properties of $AlAl_2O_4$ phase is of independent scientific interest.

References

1. A.Ya.Dan‘ko, N.S.Sidelnikova, G.T.Adonkin et al., *Functional Materials*, **10**, 2 (2003).
2. N.E.Filonenko, I.V.Lavrov, O.V.Andreeva, R.L.Pevzner, *Dokl.Akad.Nauk SSSR*, **115**, 583 (1957).
3. N.S.Sidelnikova, G.T.Adonkin, A.T.Budnikov et al., *Functional Materials*, **4**, 92 (1997).
4. E.F.Chaikovsky, in: Apparatus and Methods of X-Ray Analysis, 1st Issue, p.186, Machinostroenie, Leningrad (1967) [in Russian].
5. N.S.Greshnyakova, V.G.Alekseev, V.N.Egorov et al., in: Apparatus and Methods of X-Ray Analysis, 21st Issue, p.122, Machinostroenie, Leningrad (1978) [in Russian].
6. M.M.Borodkina, E.N.Spektor, X-Ray Analysis of Textures of Metals and Alloys, Metallurgia, Moscow (1981) [in Russian].
7. A.Ya.Dan‘ko, N.S.Sidelnikova, *Functional Materials*, **8**, 271 (2001).

Утворення фази із структурою шпінелі ($AlAl_2O_4$) на поверхні сапфіру

Н.С.Сідельнікова, М.А.Ром, О.Я.Данько, С.В.Ніжанковський, Ю.В.Сірік, С.І.Кривоногов

Виявлено явище трансформації поверхневого шару сапфіру з утворенням нової фази з кубічною структурою шпінелі ($AlAl_2O_4$) у результаті високотемпературного відбудовного відпалу. Приведено результати мікроскопічних досліджень і рентгенівського фазового аналізу шару нової фази на поверхні сапфіру для двох кристалографічних площин (0001) і ($10\bar{1}2$).