Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 39 (2013) 2259–2265
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Effects of electron-beam irradiation, a thin-Ti layer, and a BeO additive on the diffusion of titanium in synthetic sapphire

Yongkil Ahn[a], Jingyo Seo[a], Pornsawat Wathanakul[b,c], Jongwan Park[a,*]

[a]*Department of Materials Science and Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea*
[b]*Department of Earth Sciences, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand*
[c]*The Gem and Jewelry Institute of Thailand (Public Organization), Bangkok 10500, Thailand*

Received 29 July 2012; received in revised form 23 August 2012; accepted 23 August 2012
Available online 6 September 2012

Abstract

Titanium was allowed to diffuse into synthetic sapphire (α-Al_2O_3) at 1773–1923 K for 200 h in air. Specimens were prepared by four different methods. Samples were irradiated with a 10 MeV electron beam to fluencies of 2×10^{17} cm^{-2} for 1 h to induce vacancy formation. A 1-μm layer of titanium was sputtered onto sapphire samples to provide intimate contact with the diffusing elements. Ti diffusion was performed using TiO_2 powder or a mixture of TiO_2 and BeO powders in a ratio of 95:5 to take advantage of the beryllium activity. Ti diffusion was profiled using scanning electron microscope-energy dispersive X-ray spectrometry (SEM–EDX). The diffusion coefficients of Ti were as follows:

Sapphire irradiated, coated with Ti, and embedded in TiO_2/BeO mixture.

$D_{Ti} = 1.9\exp\ (-572.1 \pm 18.5\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{m^2\ s^{-1}}$,

Sapphire irradiated, coated with Ti, and embedded in TiO_2 powder.

$D_{Ti} = 1.4\exp\ (-577.4 \pm 23.3\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{m^2\ s^{-1}}$,

Sapphire irradiated, non-coated and, embedded in TiO_2 powder.

$D_{Ti} = 1.2\exp\ (-582.4 \pm 27.1\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{m^2\ s^{-1}}$,

Sapphire non-irradiated, non-coated, and embedded in TiO_2 powder.

$D_{Ti} = 9.0\exp\ (-621.4 \pm 12.4\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{m^2\ s^{-1}}$

These results demonstrate that titanium penetrated the deepest into the sapphire samples that were electron-beam-irradiated, coated with Ti, and embedded in the TiO_2/BeO mixture.

Keywords: C. Diffusion; D. Al_2O_3; D. TiO_2; Electron beam irradiation

---

1. Introduction

Corundum (α-Al_2O_3) can produce gemstones of various colors depending on the impurity atoms substituted at the Al sites. Among these, ruby and blue sapphires are precious gemstones. The crystal structure of corundum belongs to the space group D^6_{3d}, and the rhombohedral unit cell is composed of two Al_2O_3 species. The aluminum cations are linked to 6 oxygen anions in a distorted octahedron, which is about two-thirds full [1]. The ionic radius of the impurities is larger than the aluminum atom, i.e., $Cr^{3+} = 0.615$ Å, $Fe^{3+} = 0.645$ Å, $Ti^{4+} = 0.605$ Å, compared with $Al^{3+} = 0.535$ Å, in an octahedral site [2]. Ti-doped sapphires can be used in tunable solid-state lasers. These lasers emit red and near-infrared light in the range of 650–1100 nm [3]. The red color of rubies is attributed to 1000 ppma Cr^{3+}, and 50 ppma Fe^{2+}–Ti^{4+} pairs are responsible for the deep blue color of sapphires [4]. The Ti^{4+} ion is slightly larger than Al^{3+}, therefore it easily enters the corundum lattice. If Fe^{2+} and Ti^{4+} ions are located adjacent to Al sites, they interact, adjusting the ionic valence of the structure. Specifically, Fe^{2+} is converted to Fe^{3+} by losing 1 electron, and Ti^{4+} is altered to Ti^{3+} by receiving 1 electron: $Fe^{2+} + Ti^{4+} \rightarrow$

---

*Corresponding author. Tel.: +82 2 2220 0386; fax: +82 2 2298 2850.
E-mail address: jwpark@hanyang.ac.kr (J. Park).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.08.071

$Fe^{3+}+Ti^{3+}$. This process is called intervalence charge transfer (IVCT). In corundum, IVCT requires about 2.11 eV. Consequently, the absorption band at 588 nm contributes to the blue color [5].

Our previous research on the diffusion of Cr^{3+} ions in sapphire [6] found that Cr-coating and electron beam irradiation yielded the deepest penetration of Cr^{3+} ions among the three methods evaluated: coated and electron beam irradiated, electron beam irradiated only, and non-irradiated. The coating method overlaid a uniform chromium film 1 μm thick on the sapphire surface using an evaporator.

In the present work, we studied titanium diffusion in sapphire. Following our previous work, we used three methods to diffuse titanium into sapphire. Additionally, we tried mixing titanium oxide powder with beryllium oxide powder as an additive to enhance penetration. The diffusion coefficient of Be^{2+} ions in corundum was estimated to be about 10^{-11} m^2/s at 2023 K [4]. For each case, we measured the diffusion coefficients and diffusivities [$D=D_0 \; exp \; (-Q_d/RT)$] of titanium in sapphire. Finally, we compared the diffusion kinetics of the four cases using the activation energies for diffusion obtained from the calculated diffusivities.

2. Experimental procedures

Diffusion was carried out using synthetic sapphire samples. The synthetic colorless sapphire was obtained from Hrand Djevahirdjian SA (Djeva) Ltd. in Monthey, Switzerland. Specimens were cut perpendicularly in the growth direction. Samples were sliced into 16 square pieces using a diamond sawing machine. Each sample was $10\times10\times2$ mm^3. The surfaces were polished using three methods: silicon carbide cc-220 cw, cc-2000 cw abrasive paper, and alumina powder. The polished sapphires were then cleaned for 10 min in an ultrasonic bath filled with distilled water [7].

For comparison with our previous study, we pre-irradiated 12 pieces of sapphire in an electron accelerator at an electron energy of 10 MeV to fluencies of 2×10^{17} cm^{-2}. A 1 μm-thick titanium layer was coated by evaporation onto the sapphire surfaces after electron beam irradiation. A columned lump of titanium metal was packed into a $1\times1\times1$ cm^3 carbon crucible. The titanium was melted and evaporated via electron beam using the following conditions: beam current of 60 mA, voltage of 4.36 kV, and a high vacuum pressure of 3×10^{-6} Torr.

We prepared two types of titanium for diffusion: titanium oxide powder for embedding and titanium metal for evaporation. For the Ti^{4+} ion doping, titanium oxide powder and titanium metal of 99.0% purity were purchased from Duksan Pure Chemical Co. Ltd., Korea. As an additive, BeO powder of 99.0% purity was purchased from A Johnson Matthey. Diffusion experiments were performed using sapphire samples prepared by four different preparation methods: with or without electron beam irradiation, with or without Ti coating on the sapphire surface, and with samples embedded in TiO_2 powder and a TiO_2 (95%)/BeO (5%) powder mixture. The specimens embedded in powder were tightly packed into an alumina ceramic crucible with a cover. The specimens were then heated in an electric furnace in a horizontal alumina tube. The heat treatment was conducted in 50 K intervals at temperatures ranging from 1773 K to 1923 K for 200 h in air. The temperature was steadily raised by 3 K a minute and quenched at 1673 K. Cross sections of the diffused specimens were ground and polished horizontally.

3. SEM-EDS and LA-ICP-MS analysis

Titanium diffusion in the samples was investigated using a scanning electron microscope (SEM; Nova Nano 200, FEI Co.). The depth profiles of diffused titanium were measured by energy dispersive X-ray spectrometry (EDX) (EDAX Inc.). Fig. 1 shows the positions of the detecting points on the cross-section of the diffused samples. To detect diffused elements, we measured the diffused content (ppma) of beryllium and titanium at these positions using a laser ablation inductively coupled plasma mass spectrometer (7500 series LA-ICP-MS, Agilent Technologies Company) at the Gem and Jewelry Institute of Thailand.

4. Results and discussion

Fig. 2 shows an SEM image of the sapphire samples after diffusion. The cross-sectioned surface of the sapphires was distinguished by Ti- and Al-rich oxide layers, along with the original interface. The highlighted horizontal line was used for line scanning by EDS. The depth profiles of diffused titanium were obtained by line-scanning from the highlighted line toward an aluminum-rich surface. We analyzed the titanium counts based on the depth profile from EDS.

Fig. 3 depicts the Ti profile in sapphire samples heated at 1773 K for 200 h. The Ti concentration versus diffusion depth (10^{-6} m) was consistent with a Gaussian-type distribution. Fig. 3 was converted into log (Ti counts) versus x^2 (square of

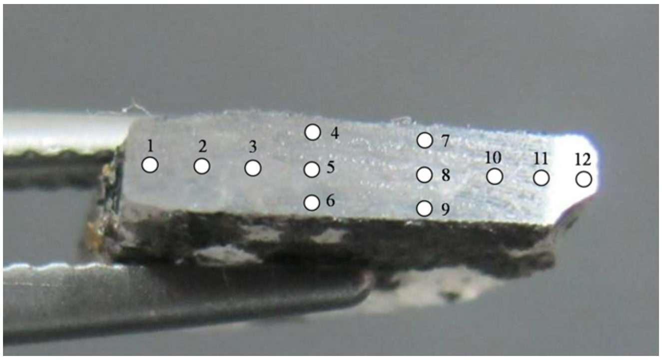

Fig. 1. Positions of the detecting points on the cross-section of the diffused samples measured by LA-ICP-MS.