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High temperature microhardness of Zr-, Sc- and Al-doped rutile crystals

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Abstract

Vickers microhardness of Zr-, Sc- and Al-doped rutile crystals were measured from room temperature to 900 °C. In the high temperature range where the crystal quality is influenced, the doped crystals had a hardness of more than 10% higher than that of the undoped crystal. The crystal quality was found to be improved by solid solution hardening.

Keywords: Rutile crystals; Microhardness; Zirconium doping; Aluminium doping; Scandium doping

1. Introduction

The floating zone method is well suited for preparing large refractory crystals. The crystals, however, are grown under a steep temperature gradient, and generally contain defects such as dislocations and subgrain boundaries. The crystal quality can be presumed to be influenced by plastic deformation, movement and aggregation of dislocations, as a result of thermal stress. Therefore, useful information for improving the crystal quality would be obtained by examining plastic deformation of the crystal.

Rutile single crystals (TiO_2) are chosen as samples because the crystal quality strongly depends on the growth conditions. Rutile crystals are grown in a low oxygen partial pressure, 10^{-1}–10^{3} Pa, to suppress formation of subgrain boundaries, and annealed in an oxidation atmosphere after the growth to remove oxygen vacancies [1]. Recently, by doping ZrO_2, Sc_2O_3 and Al_2O_3, it was possible to grow high quality crystals even in an oxidizing atmosphere [2,3].

2. Experimental

TiO_2 crystals were prepared for hardness measurements by the floating zone method using an infrared convergence-type furnace. High purity TiO_2 powder (>99.9%) was used as a raw material. The dopants were 0.4 mol.% ZrO_2, 0.1 mol.% Sc_2O_3 and 0.1 and 0.3 mol.% Al_2O_3. The growth rate was 0.5 cm h^{-1}. The upper and lower shafts were counter rotated at a rate of 30 rpm. The growth atmosphere was an oxygen flow of 2 l min^{-1}. The details were described elsewhere [1–3].

The crystals obtained were cut into rectangular blocks, $5\times5\times10$ mm^3, which consisted of (001) and (110) planes of the tetragonal crystal lattice. The planes were mirror-like polished using 0.3 μm almina powder.

Indentation experiments were carried out from room temperature to 900 °C in air, using a micro-hardness tester (Nikon Ltd., QM-2) [4]. A saphire Vickers indenter was used. The load was 200 g for 1–100 s. The hardness was obtained from an average value of several measurements.

3. Results and discussion

It is well known that dislocation-free GaAs crystals are grown as a result of indium doping (see for example Ref. 5). Recently, in the LaB_6 crystal growth, even subgrain boundaries in which the misorientation was up to 3 deg were removed as a result of solid solution hardening [4,6,7]. Therefore, the high temperature hardness of Zr-, Sc- and Al-doped rutile crystals was mea-

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sured and the origin of the improvement in the crystal quality was examined by comparison with the hardness of the undoped crystal.

Fig. 1 shows the hardness for the ⟨110⟩ orientation on the (001) plane. The undoped crystal had a hardness which consisted of four linear parts. There are three inflection points at 100, 400 and 700 °C, which are generally observed when using a single crystal as a sample. The sample did not deform plastically below the lowest inflection point, >100 °C, because only cracks, no slip bands, were observed around the indentations on the samples. The plastic deformation occurred above the lowest inflection temperature, >100 °C, which was confirmed from the slip bands around the indentations. Above the highest inflection temperature, >700 °C, dominant mass transfer process is probably a result of bulk diffusion because Tammann temperature is about 0.5 °C in oxides. Therefore, in this temperature range, the crystal quality would be determined as a result of relaxation of thermal stress.

The Zr-doped crystal has almost the same temperature dependence of the hardness as the undoped crystal, as shown in Fig. 1. Three inflection points were also observed at the same temperatures, 100, 400 and 700 °C. However, the difference in the hardness increased with increasing temperature, and is 10% higher above the highest inflection temperature. In the LaB_6 crystal growth, a 10% increase in hardness removed perfectly the boundaries from the crystal [4]. In the case of tungsten-doped TiC crystals, the boundaries were decreased to one fourth by 14% increase in the hardness [8]. Therefore, it is suggested that rutile crystals were improved in quality by a 10% increase in the hardness due to solid solution hardening.

The hardness of the Sc-doped crystal is also shown in Fig. 1. The three inflection points near 300, 500 and 800 °C, are 100–200 °C higher than in the undoped and Zr-doped crystals. Above the lowest inflection temperature, slightly above 300 °C, where the slip bands were observed, the hardness did not decrease as much as in the case of the undoped and the Zr-doped crystals. A similar change in the hardness is also observed in Al doping, as shown in Fig. 1. Therefore, this change in the hardness is because the strain of the crystal lattice increased as a result of the oxygen defects introduced by doping the trivalent ions, Sc^{3+} and Al^{3+}. The hardness decreased rapidly above the middle inflection point, 600 °C, which means that the lattice distortion started to relax. Above the highest inflection point, 800 °C, the crystal had a 30% higher hardness than that of the undoped one. Therefore, the solid solution hardening was also confirmed in the crystal which was improved in quality because of Sc doping.

In the case of doping 0.1% Al_2O_3, the inflection temperatures increased more than in the case of 0.1% Sc doping. The lowest and middle inflection temperatures increased by 50 °C and 300 °C, respectively. The highest inflection point could not be observed in the temperature range considered. Increasing the amount of Al_2O_3 to 0.3% further increased the hardness, as shown in Fig. 1. The hardness measurements suggest that Al doping is most effective for improving the crystal quality.

Figs. 2 and 3 show the time dependence of the hardness of the undoped and Sc-doped crystals, respectively. The hardness did not decrease in spite of increasing the indentation time below the lowest inflection temperatures (<100 °C and <300 °C in both cases). The crystals creeped above the lowest inflection temperatures. The gradient of decrease in the measured

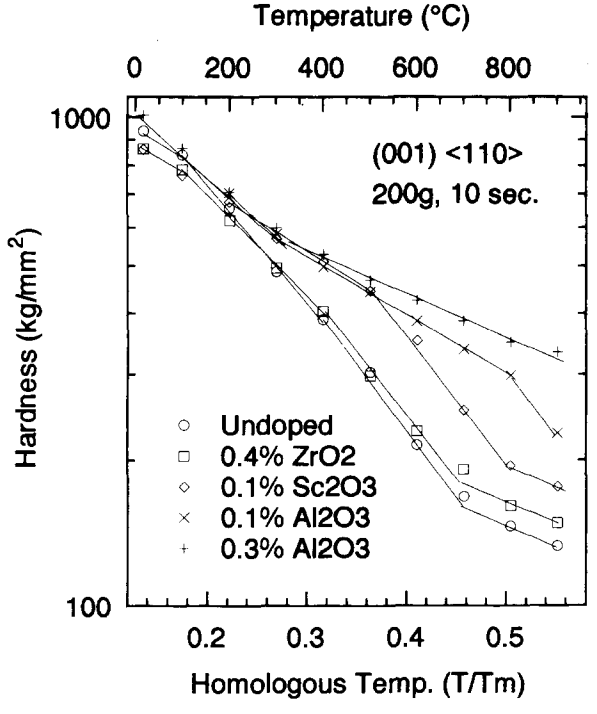

Fig. 1. Vickers micro-hardness on the (001) planes.

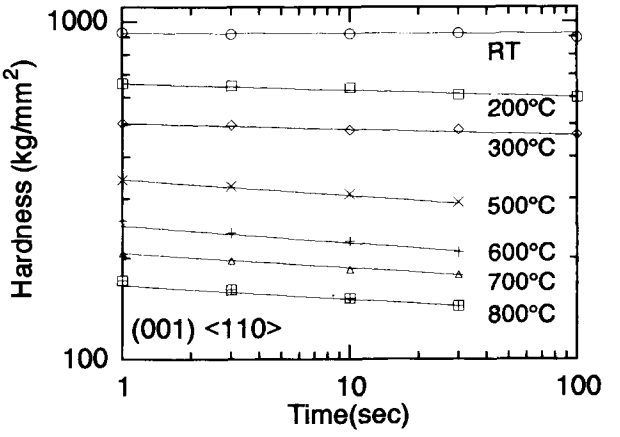

Fig. 2. Time-dependence of the hardness of the undoped rutile crystal. The load was 200 g for 10 s.

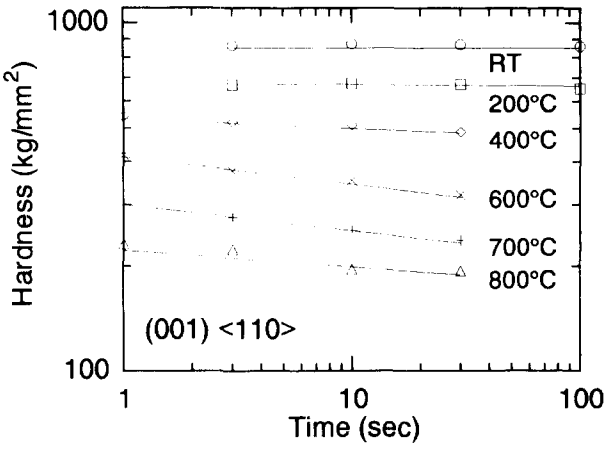

Fig. 3. Time–dependence of the hardness of the Sc-doped rutile crystal. The load was 200 g for 10 s.

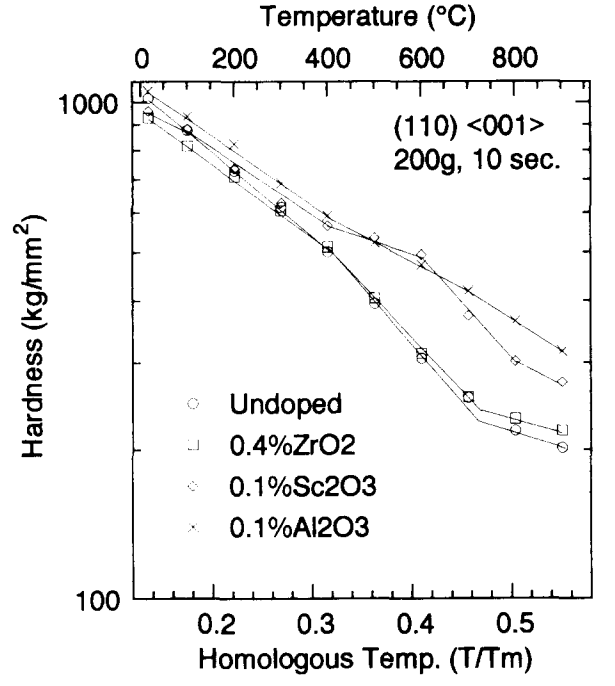

Fig. 4. Vickers micro-hardness on the (110) planes.

hardness changed at 100, 400 and 650 °C in the undoped crystal, and at 300, 500 and 750 °C in the Sc-doped crystals, which are consistent with the inflection temperatures shown in Fig. 1. Above the highest inflection temperature where the crystal quality is influenced, the activation energy for the creep in the undoped crystal is obtained by using the following formula for a constant creep process:

$$H^{-m} = A \exp(-Q/RT)t$$

where H, Q, R, T and t are hardness, activation energy, gas constant, temperature and time, and m and A are constants. The activation energy obtained is 86 kcal mol^{-1}. This value is a little higher than the activation energies for self-diffusion f Ti and oxygen, 56 and 66 kcal mol^{-1}, respectively [9,10]. The activation energy, however, in the Sc-doped crystal was 67 kcal mol^{-1} by using the hardness at 900 °C, which is consistent with that for self diffusion of oxygen.

Fig. 4 shows the hardness on the (110) plane, being different from that of the (001) plane. Each sample had a hardness of 50–55% higher, compared with the (001) measurements shown in Fig. 1. Three inflection points were observed at the same temperatures. All the doped crystals had a hardness of more than 10% higher than the undoped crystal. The solid solution hardening was likewise confirmed in the measurements on the (110) plane.

4. Conclusion

Rutile crystals which were improved in quality as a result of Zr-, Sc- and Al-doping had a hardness of more than 10% higher than the undoped crystals around the Tammann temperature. It was found that the crystal quality was influenced strongly by plastic deformation because of thermal stress.

In addition, the high temperature hardness measurements revealed that it is not difficult to remove subgrain boundaries from crystals in the floating zone growth because the boundaries were removed, or decreased remarkably, by increasing the hardness by only about 10%.

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