Ceramics International 24 (1998) 189–198

PII: S0272-8842(97)00001-1
0272-8842/98 $19.00 + .00

Mechanical Properties of Titanium Implanted Polycrystalline Alumina and Sapphire Determined by Nanoindentation

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(Received 15 July 1996; accepted 25 November 1996)

Abstract: The effects of titanium ion implantation on structural and mechanical properties of single crystal and polycrystalline α-alumina were studied. Grazing angle X-ray diffraction (GXRD) allowed the identification of structural alterations. Surface morphology was observed directly using scanning electron microscopy (SEM), elastic and plastic properties of the implanted layers (of which the thickness is about 100 nm) have been characterised by microprobe investigation. Results of the hardness and Young's modulus, determined by nanoindentation technique and the physicochemical study, have allowed us to correlate elastic and plastic property modifications with microstructure state of implanted ceramics and after annealing. Ion implantation plus thermal annealing were found to be favourable for the improvement of mechanical properties. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Ion implantation is a technique of surface processing which permits the creation of a fine layer of determined composition, with modifications in electrical and mechanical properties. Improvement of mechanical properties (hardness, Young's modulus) of ceramics by ion implantation is possible if a number of experimental conditions are verified. Taking into account that the implanted zone is very thin, the most adapted technique to determine mechanical properties such as the hardness and the Young's modulus is nanoindentation. By the continuous measure of the load and the depth of penetration, this technique allows to determine the evolution of these parameters for a penetration in depth of about some tens of nanometres. Conventional tools are also used to estimate the hardness of the implanted material, such as Vickers or Knoop indenter. This type of measure includes the hardness of the substrate because of the very fine thickness of the implanted zone.

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Burnett and Page[1] have shown that at doses where damage is introduced but the lattice remains crystalline during implantation, the hardness increases with the dose due to radiation and/or solution hardening. When the dose increases to result in a buried amorphous layer, the hardness begins to decrease as the thickness of the layer increases. When the amorphous layer extends to the surface, the hardness is less than that of the unimplanted region.[2] In the case of zirconium implanted alumina 2×10^{17} ions cm^{-2} (energy 170 keV) the hardness of the amorphous layer was decreased by nearly 60%.[3]

Thermal annealing can often be used to restore crystallinity to the damaged near-surface region, and additionally, metastable solid solutions can be produced. For a number of oxide materials, the annealing behaviour has been studied in detail using both Rutherford back-scattering–ion channelling techniques and transmission electron microscopy.[4] It has been found that the near surface remained crystalline during implantation at room temperature, and the behaviour during thermal annealing in air was consistent with the expectations of the equilibrium phase diagram (i.e. Cr was incorporated into solid solution, but Ti and Zr were observed to precipitate). Other results[5–8] indicated that the chemistry of the implanted ion was important in determining the microstructure during implantation and they also observed the formation of oriented precipitates during annealing and found that the nature of the precipitates depends strongly on the annealing environment.

The aim of this study is to investigate the effects of titanium ion implantation and of post-annealing treatments on the structure and mechanical properties of single crystal and polycrystalline α-alumina by nanoindentation technique in combination with measurements of the hardness and Young's modulus, grazing-angle X-ray diffraction (GXRD) and scanning electron microscopy (SEM)

2 EXPERIMENTAL TECHNIQUES

2.1 Ion implantation

Polycrystalline alumina (α-Al_2O_3, Matroc, purity 99.95%) was used. The average grain size is 3 μm. The samples were mechanically polished to a 1-μm surface finish (average roughness = 0.02 μm) and annealed in air for 1 h at 1200°C to relax the majority of stresses induced by polishing and to clean the surface. Samples were implanted at room temperature with 2×10^{16} and 1×10^{17} ions Ti cm^{-2} at 170 keV. The annealing was carried out at temperatures of 800, 1000 and 1200°C. Over this range of temperatures different phenomena are observed, such as the recovery of defects, the crystallization of the amorphous layer, the formation of new chemical phase or solid solution.[4,9,10]

2.2 Nanoindentation

Measurements of mechanical property are very delicate in the case of implanted materials because of the low thickness of the implanted layer, that is about 100 nm. They have been possible using a nanoindenter®II (Nano Instruments Inc., Knoxville, TN, USA).[11,12] By this technique, which allows a continuous load–displacement measurement, the hardness and the Young's modulus in all the zone concerned by the ion implantation can be calculated.

Mechanical characteristics of implanted samples were measured from loading and unloading cycles of curves of indentation load–displacement (Fig. 1) to four different depths. The loading portions of the test were done at a constant displacement rate of about 5 nm s^{-1}.

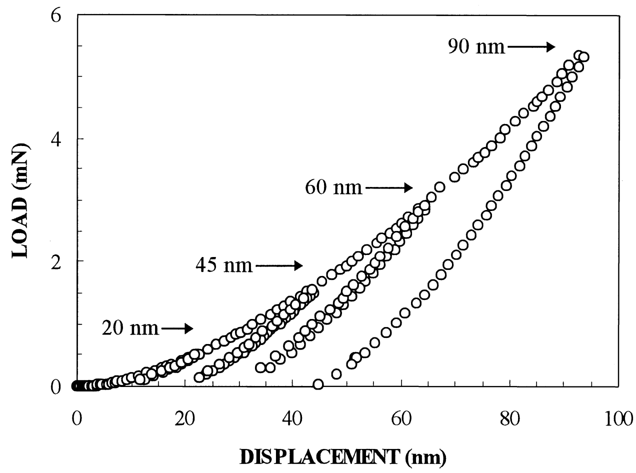


Fig. 1. Load vs indenter displacement for four depths experiment performed on alumina.

3 RESULTS AND DISCUSSION

3.1 Polycrystalline alumina

3.1.1 Alumina implanted with 2×10^{16} ions Ti cm^{-2}
For low implantation dose of titanium where the near-surface remains crystalline, the hardness and the Young's modulus remain unaltered (Fig. 2). Physicochemical analyses do not reveal formation of compounds over the surface. After annealing to 800°C, the hardness and the Young's modulus remain identical to unimplanted alumina. An annealing temperature greater than 800°C (1000 and 1200°C), decreases the hardness and the Young's modulus due to the presence of TiO_2 observed on GXRD diagrams (Fig. 3), and also observed by SEM.

3.1.2 Alumina implanted with 1×10^{17} ions Ti cm^{-2}
For the higher dose, and without annealing, the values of the mechanical properties of implanted alumina are lower than those of the unimplanted samples. For an indentation depth of 45 nm, decreases of about 24% for the hardness and 10% for the Young's modulus are observed with respect to the unimplanted alumina (Fig. 5) due to the fact of the presence of transition alumina (γ-Al_2O_3). Annealing to 800°C conduct to the decrease of mechanical properties (H, E) due to the fact of the presence of TiO_2 detected by GXRD (Fig. 6), and also observed by SEM. For the higher temperature (1000 and 1200°C) where the annealing produces an increase of TiO_2 concentration (Fig. 7), a decrease of about 80% in hardness and 55% in Young's modulus are observed at a depth of 45 nm. The near-vertical unloading curve allows the determination of the surface region of a TiO_2

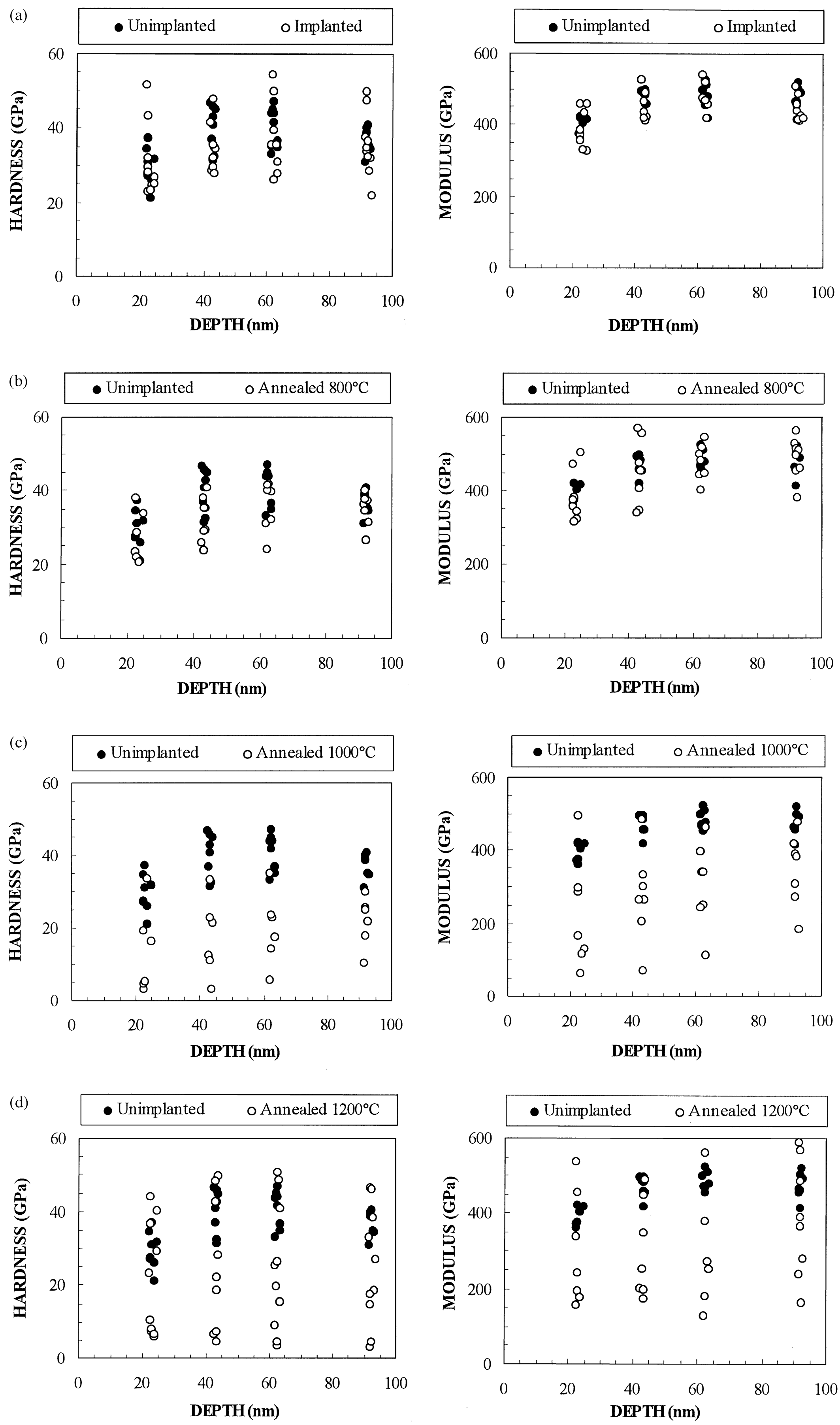


Fig. 2. Hardness and Young's modulus vs depth for unimplanted and implanted alumina. (a) Unannealed, annealed at (b) 800, (c) 1000 and (d) 1200°C (dose 2×10^{16} ions Ti cm^{-2}).

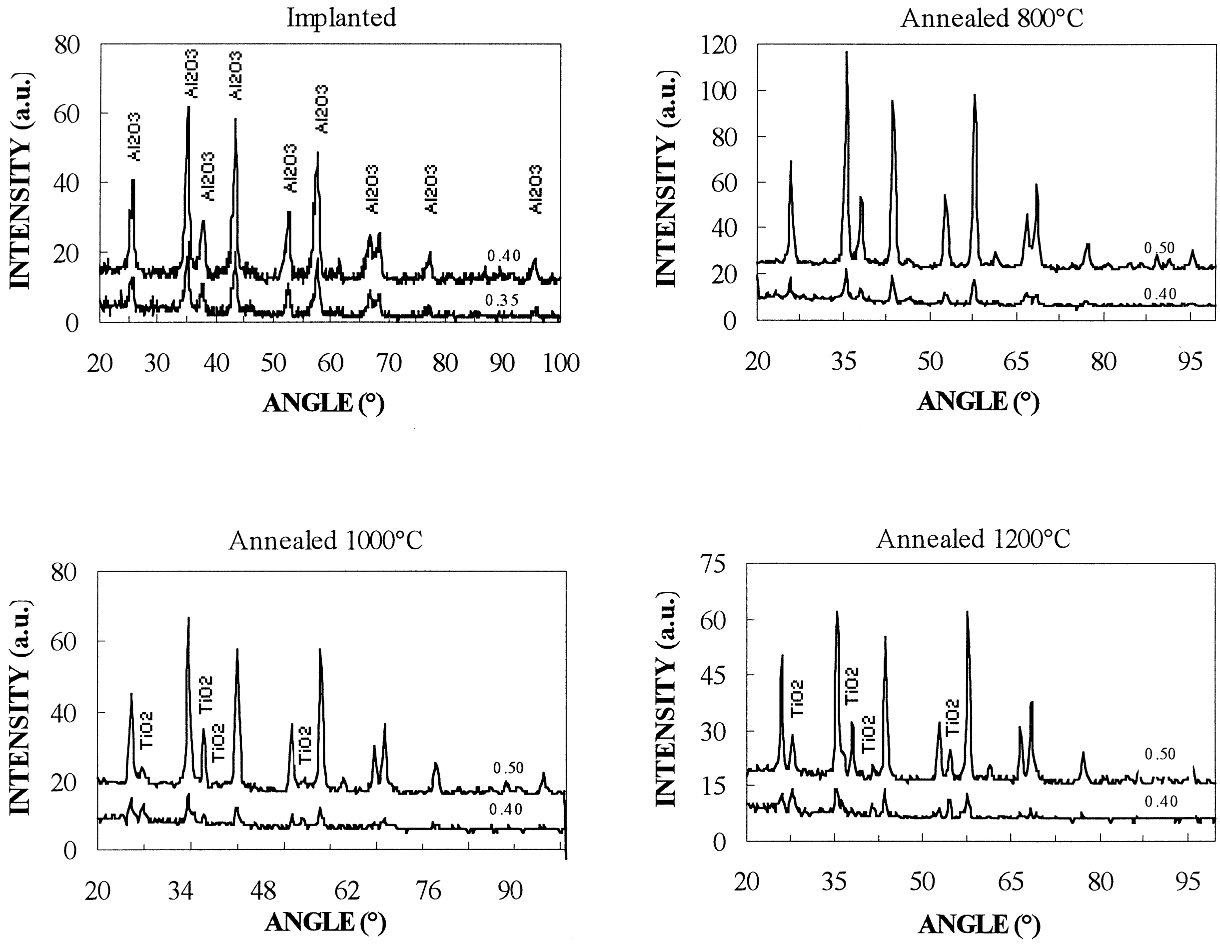


Fig. 3. GXRD spectra of implanted alumina at 2×10^{16} ions Ti cm^{-2} and annealed.

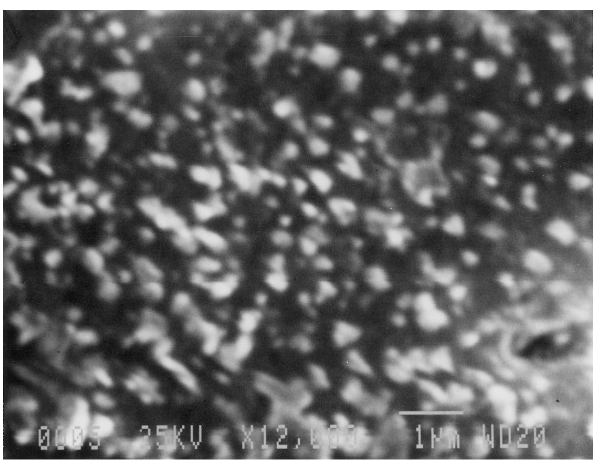


Fig. 4. SEM micrograph of titanium implanted alumina 2×10^{16} ions Ti cm^{-2} and annealed at 1200°C.

plastic layer (Fig. 8), in agreement with results measured by Mayo *et al.*[13]

3.2 Sapphire

3.2.1 Sapphire implanted with 2×10^{16} ions Ti cm^{-2}

Figure 9 shows the change in the hardness and Young's modulus vs depth at low dose for implanted sapphire. For an indentation depth of 45 nm, a decrease of about 14% for the hardness of the layer implanted is observed but the Young's modulus is identical to the unimplanted sapphire. The hardness and Young's modulus measured after an annealing to 800°C and at 1000°C are identical to those of the unimplanted sapphire. After an annealing to 1200°C, the mechanical properties increase compared to the values of the unimplanted sapphire (about 17% for the hardness and 11% for the Young's modulus).

Figure 10 shows the two types of curve that were commonly seen for the lower penetration depth. Figure 10(a) shows a perfectly elastic indentation to a depth of about 20 nm in which, on unloading, almost complete recovery of the indenter displacement was observed on unimplanted sapphire. For the 30 nm indentations, a sudden displacement discontinuity in the curve during a loading segment occurs at a given depth. This discontinuity is the apparent yield point at which plastic deformation begins. A study by Hainsworth[14] and O'Hern[15] supports this conclusion. Figure 10(b) shows a second type of curve that was seen after titanium implantation at 2×10^{16} ions Ti cm^{-2}, for the 20 nm

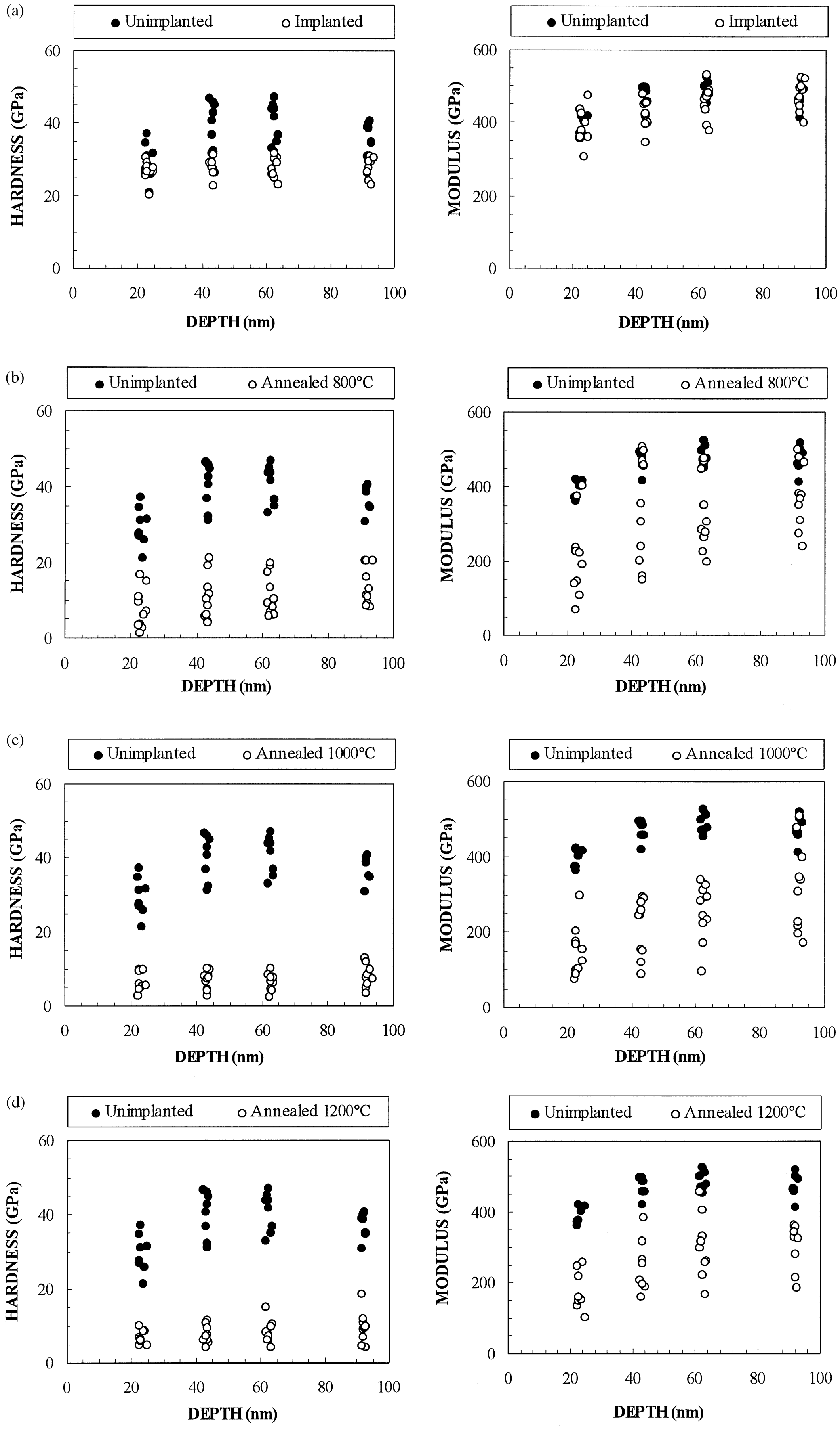


Fig. 5. Hardness and Young's modulus vs depth for unimplanted and implanted alumina. (a) Unannealed, annealed at (b) 800, (c) 1000 and (d) 1200°C (dose 1×10^{17} ions Ti cm^{-2}).

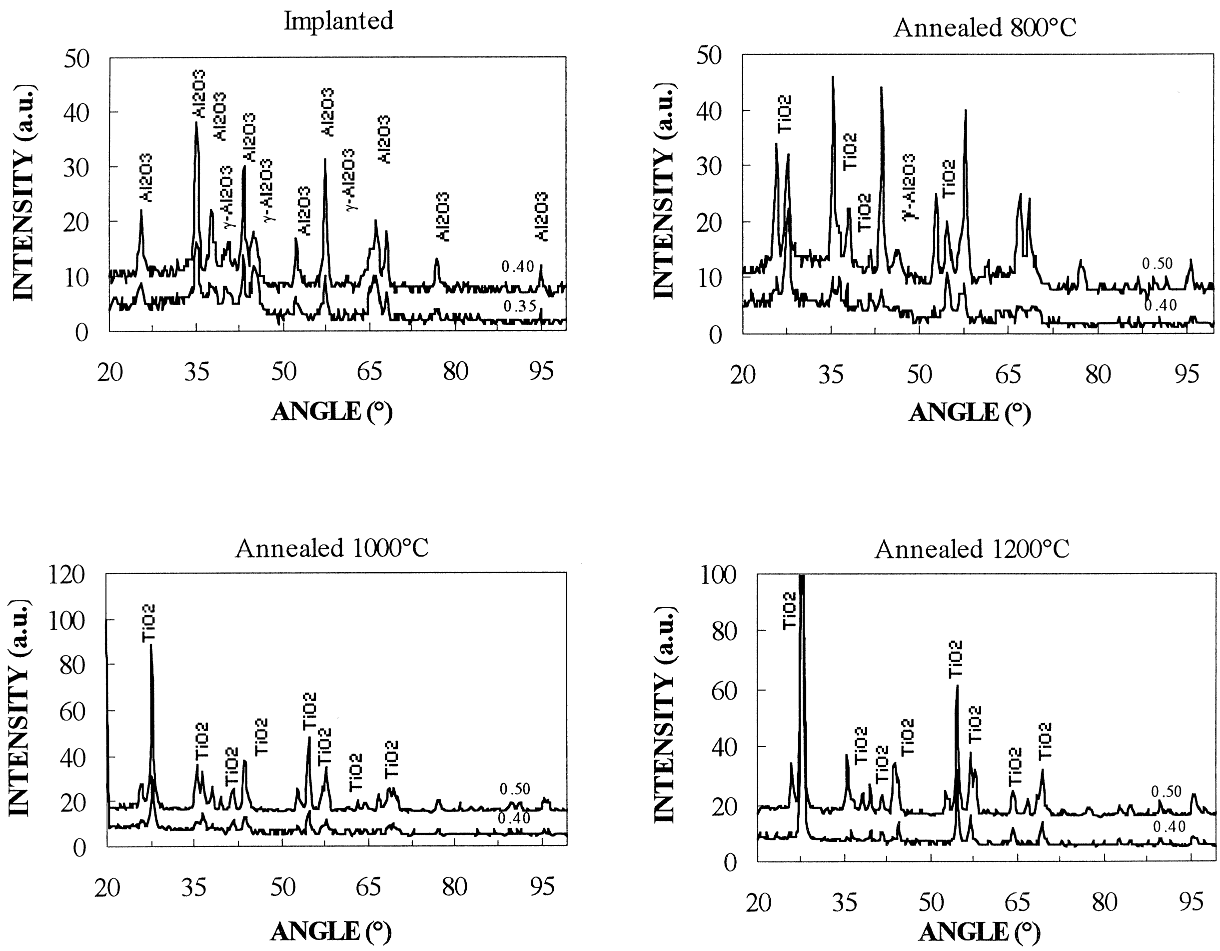


Fig. 6. GXRD spectra of implanted alumina at 1×10 ions Ti cm^{-2} and annealed.

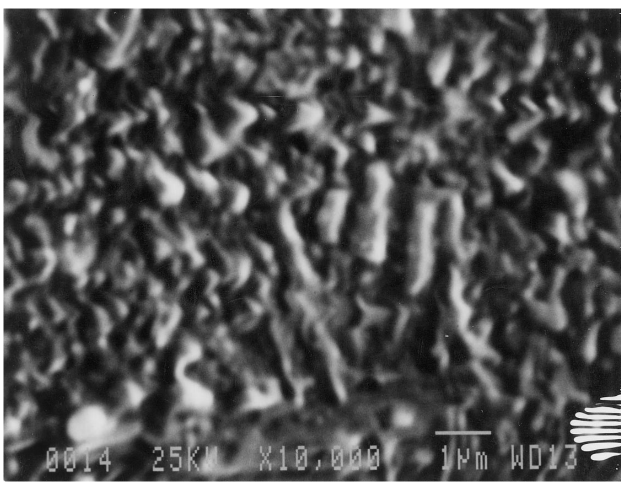


Fig. 7. SEM micrograph of titanium implanted alumina 1×10^{17} ions Ti cm^{-2} and annealed at 1200°C.

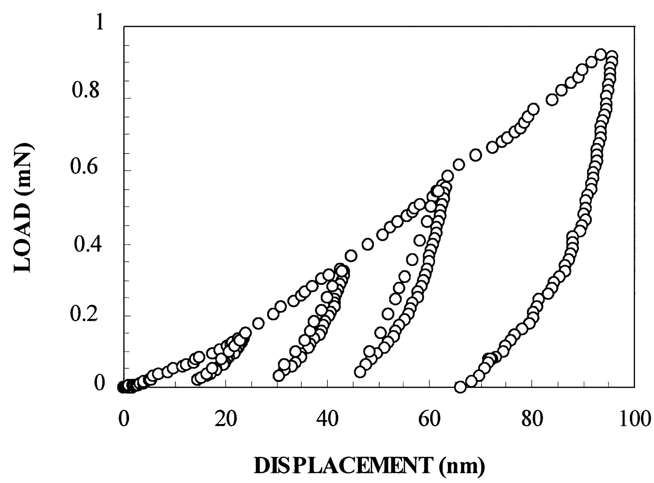


Fig. 8. Load vs displacement for experiment performed on alumina implanted at 1×10^{17} ions Ti cm^{-2} and annealed at 1200°C.

an elasto-plastic behaviour was observed, and for the 30 nm, the implanted sapphire shows no displacement discontinuity that can be due to the high density point defects and dislocation loops produced by implantation.

3.2.2 Sapphire implanted with 1×10^{17} ions Ti cm^{-2}
Figure 11 shows the change in the hardness and Young's modulus with depth and high dose for implanted sapphire. For the higher dose, the values of the mechanical properties of the implanted

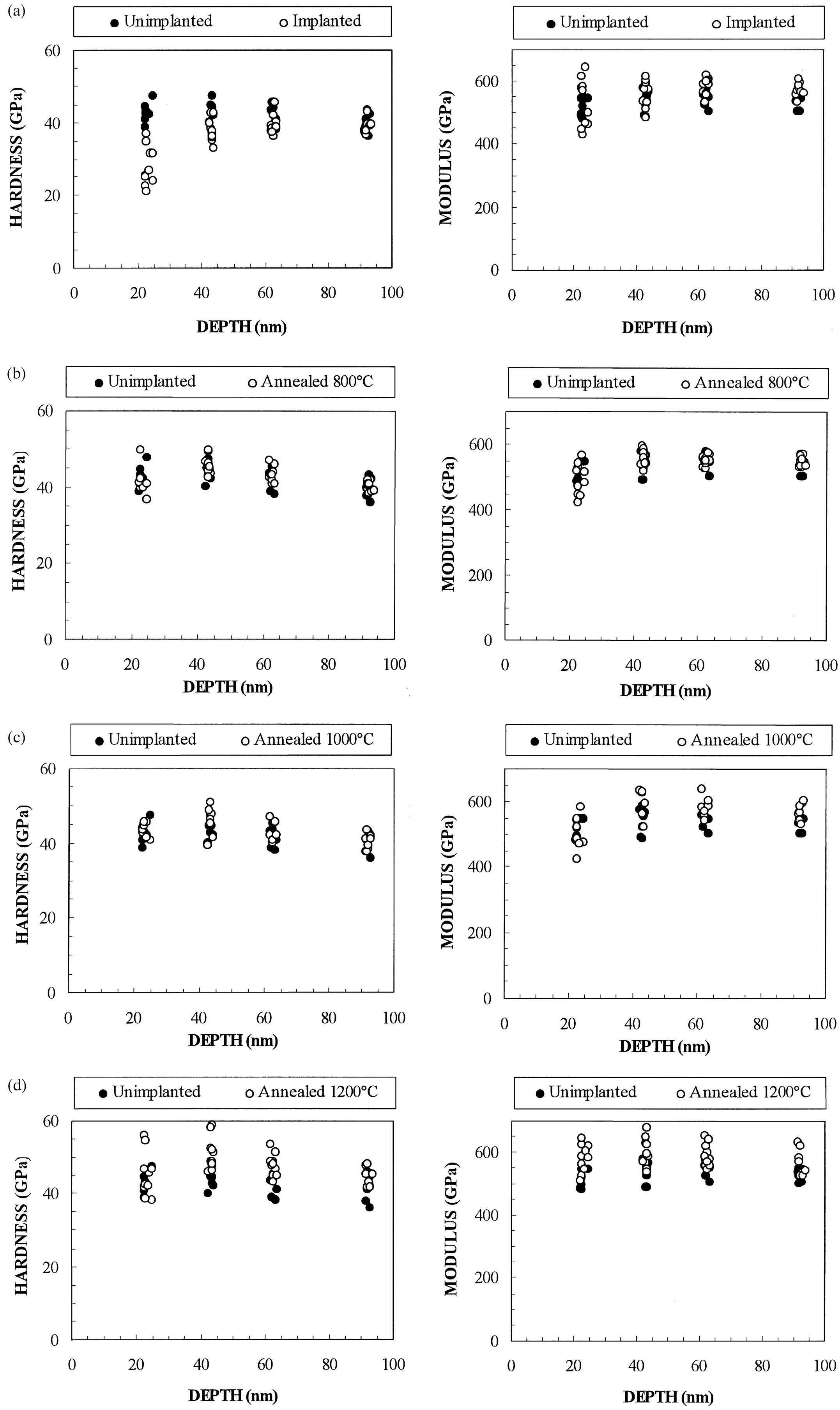


Fig. 9. Hardness and Young's modulus vs depth for unimplanted and implanted sapphire. (a) Unannealed, annealed at (b) 800, (c) 1000 and (d) 1200°C (dose 2×10^{16} ions Ti cm^{-2}).

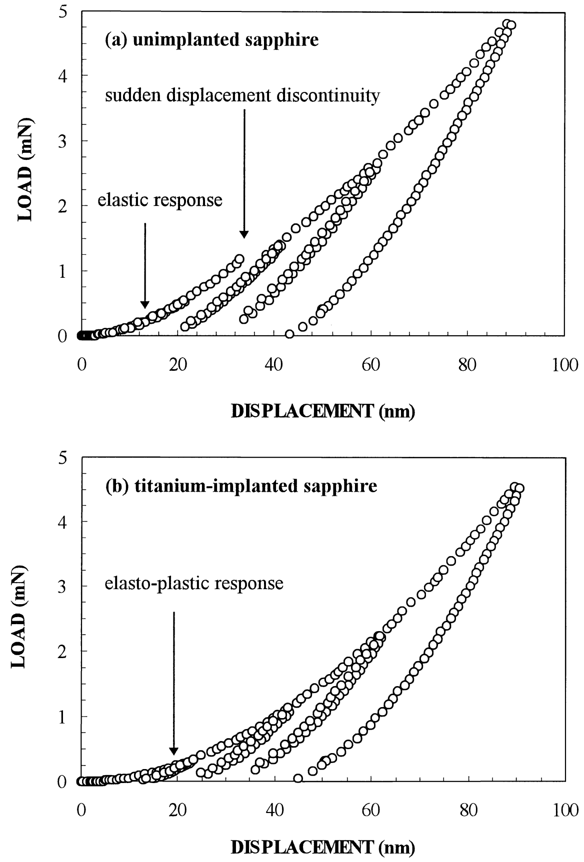
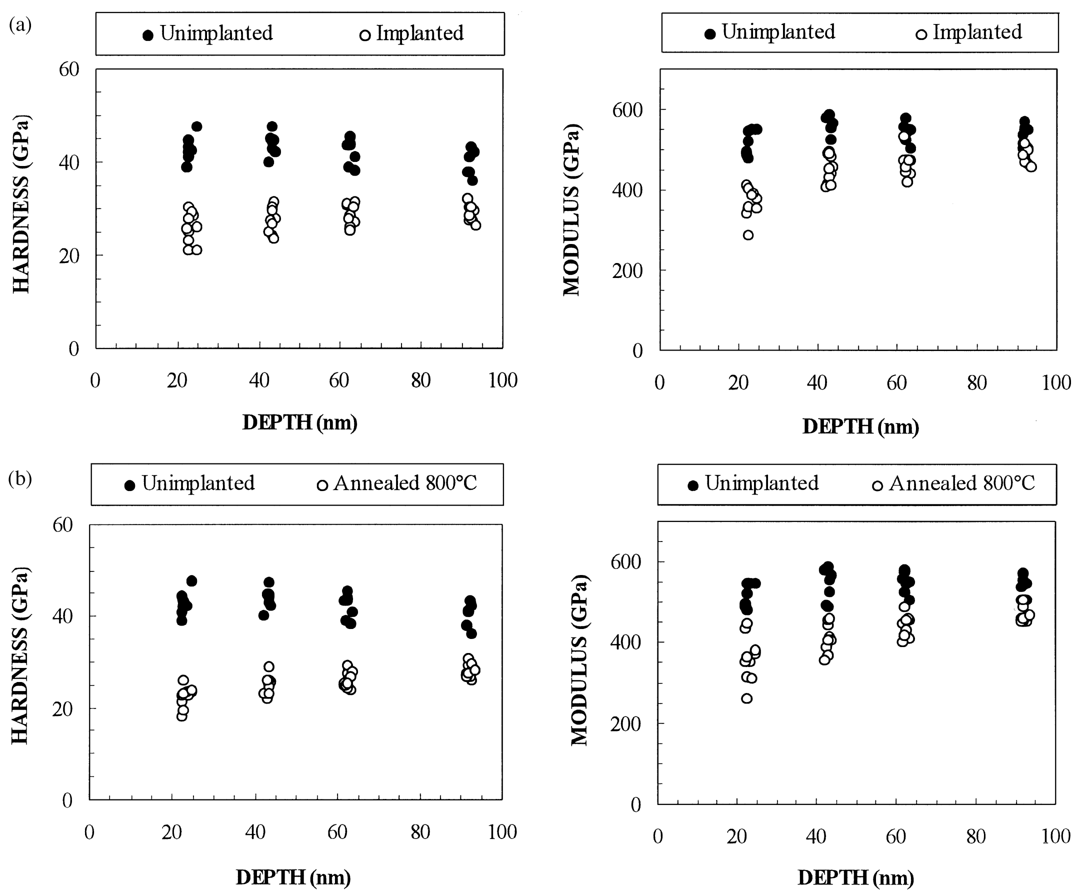


Fig. 10. Experimental curves of load vs displacement performed (a) on unimplanted sapphire and (b) sapphire implanted 2×10^{16} ions Ti cm^{-2}.

sapphire are lower than those of the unimplanted samples. For an indentation depth of 45 nm, decreases of about 37% for the hardness and 17% for the Young's modulus are observed with respect to unimplanted sapphire. After annealing at 800 and 1000°C, the hardness and the Young's modulus remain lower than those of unimplanted sapphire. Mechanical property values (H and E) are dispersed after an annealing to 1200°C, due to the fact that the layer would not be homogeneous but composed of several strata.

4 CONCLUSION

The purpose of this work has been to characterize mechanical properties of implanted ceramics and those annealed in air. The results on physicochemical and structural characterizations observed in function of treatment conditions that we have presented, have allowed us to understand the evolution of mechanical properties, hardness and Young's modulus obtained by the nanoindentation technique. It has been shown in the experimental results that dispersion is more important in the case of polycrystalline alumina, due to the presence of grain boundaries and to the variation of mechanical properties with grain orientation. In



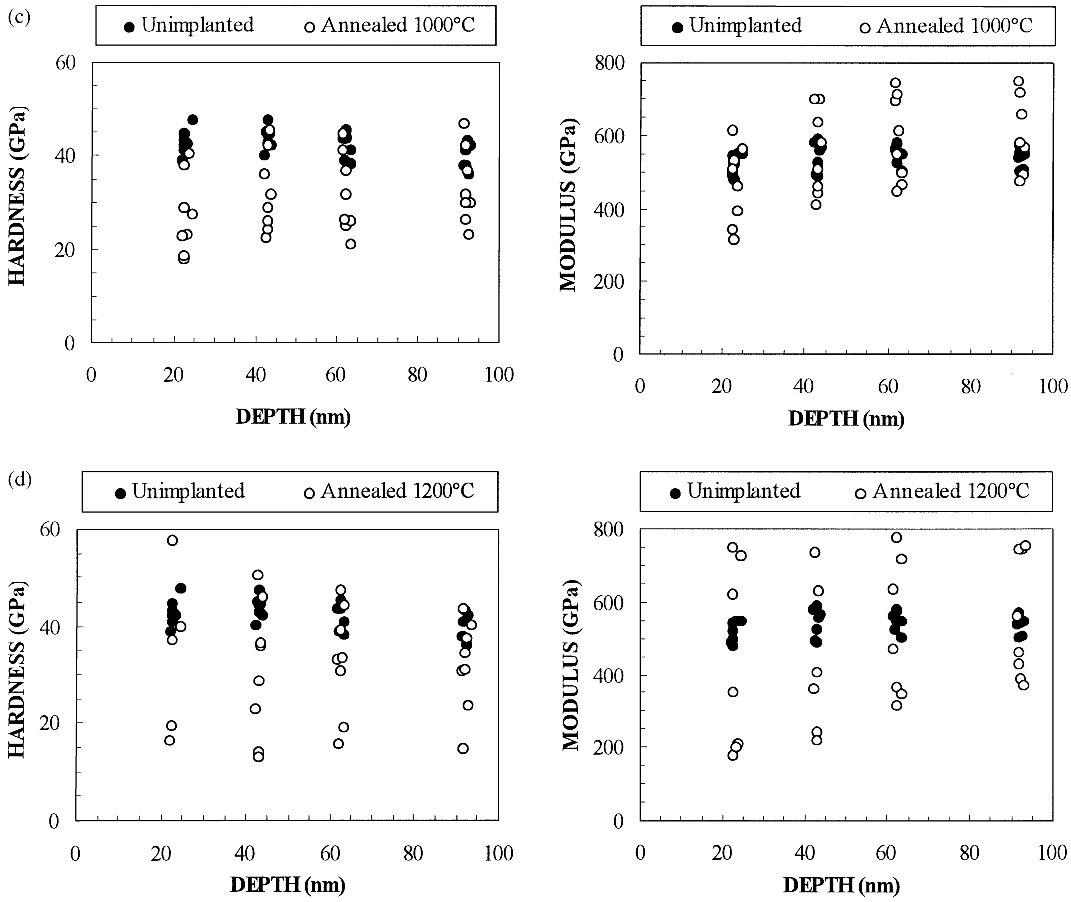


Fig. 11. Hardness and Young's modulus vs depth for unimplanted and implanted sapphire. (a) Unannealed, annealed at (b) 800, (c) 1000 and (d) 1200°C (dose 1×10^{17} ions Ti cm^{-2}).

the case of the low dose implantation and after annealing to different temperatures, it has been equally observed a largest dispersion of hardness and Young's modulus on polycrystalline alumina than in a single crystal. For the higher dose implantation and for annealing temperatures greater than 800°C, the dispersion of the results is more important for the sapphire. This would be due to the presence of at least two layers, one strongly damaged in surface and another, at a greater depth, rich in implanted atoms. Only the physicochemical and structural analysis that would be done can explain common points and the differences between the two materials.

Results of mechanical property measurement obtained by using nanoindenter techniques and the physicochemical study have allowed us to correlate elastic and plastic property modifications with microstructure state of implanted ceramics and after annealing. Under conditions that we have used, the modifications observed in mechanical properties result from both the microstructure formed in the near surface and the presence of residual stresses correlated to a damaging degree.

ACKNOWLEDGEMENTS

The authors wish to thank DRET (Direction des Recherches Etudes Techniques) for their financial support. They are also very grateful to J. Bigarre (Ecole Centrale de Lyon) who performed GXRD tests.

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