

Pb Compatibility in Ion Implanted Zircon

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Zircon ($I4_1/amd$, $Z = 4$), $ZrSiO_4$, has been widely used in age dating of crustal events due to its widespread distribution in the continental crust and tendency to concentrate trace elements, particularly lanthanides and actinides. Because of the importance of U-Th-Pb isotopic dating of zircon in interpreting crustal events, it is important to understand the equilibrium and kinetic behavior of both the parent (U, Th) and daughter (Pb) elements in the zircon matrix. Usually, Pb exhibits incompatible behavior toward zircon because of unmatched ionic size and charge balance, and only Pb^{4+} is conducive to substitution for Zr^{4+} in the zircon lattice. Natural zircons concentrate U and Th during growth and tend to reject Pb, so most Pb in zircons is produced in situ from decay. However, some non-radiogenic Pb (~2 ppb to 80 ppm) does exist even in zircons apparently unaffected by contamination or metamictization [1]. It is possible that radiogenic lead atoms assume the same valence as common Pb incorporated while zircon crystallized in which case the two are indistinguishable. Therefore, the incorporation of Pb in zircons during its growth and its diffusion later over geologic time, unless properly recognized, pose risk of overestimation or underestimation of ages by the U-Pb technique.

In this study, the microstructure evolution of zircons upon ion damage and the compatibility of Pb in zircon matrix have been studied by transmission electron microscopy after 300 keV Pb^+ ion implantation at room temperature. At an ion fluence of 1×10^{16} ions/cm² (Fig. 1A), a continuous amorphous layer with a thickness of ~155 nm has been created by Pb^+ implantation as a result of radiation damage above the critical damage level (0.4 ~0.5 dpa) for amorphization. In addition to the amorphous layer, a Pb nanoparticle layer with a thickness of ~100 nm formed in zircon matrix implanted by 1×10^{17} ions/cm², as observed by high-resolution TEM (Fig. 2A), electron and X-ray diffractions. The Pb nanocrystal formation in zircon matrix is further evidenced by a high-angle annual dark field scanning TEM (HAADF-STEM) image (Fig. 2B). At a lower ion fluence, no evidence of nanocrystal formation has been found (Fig. 3A), and STEM-EDX scanning along the white line in Fig. 3A indicates a Gaussian distribution of Pb^+ ions in zircon matrix (Fig. 3B) with a peak concentration of ~3 atom % at a depth of ~76 nm, close to the ion range (~67 nm) and distribution of 300 keV Pb^+ in amorphous zircon matrix, as calculated by SRIM-2000 code. This result suggests that no significant Pb^+ ion redistribution occurs a result of subsequent ion implantation due to a slow diffusion in zircon matrix at room temperature. When the ion concentration exceeds ~3.5 atom% (at 10^{17} ions/cm²), Pb nanoparticles precipitated at room temperature from the amorphous zircon matrix. This suggests that 3.5 Pb% is above the solubility of Pb in zircon, and this leads to the formation of Pb nanoparticles [2].

[1] E. B. Watson *et al.*, Chemical Geology 141, (1997) 19.

[2] This work was supported by USDOE under grant DE-FG02-97ER45656.

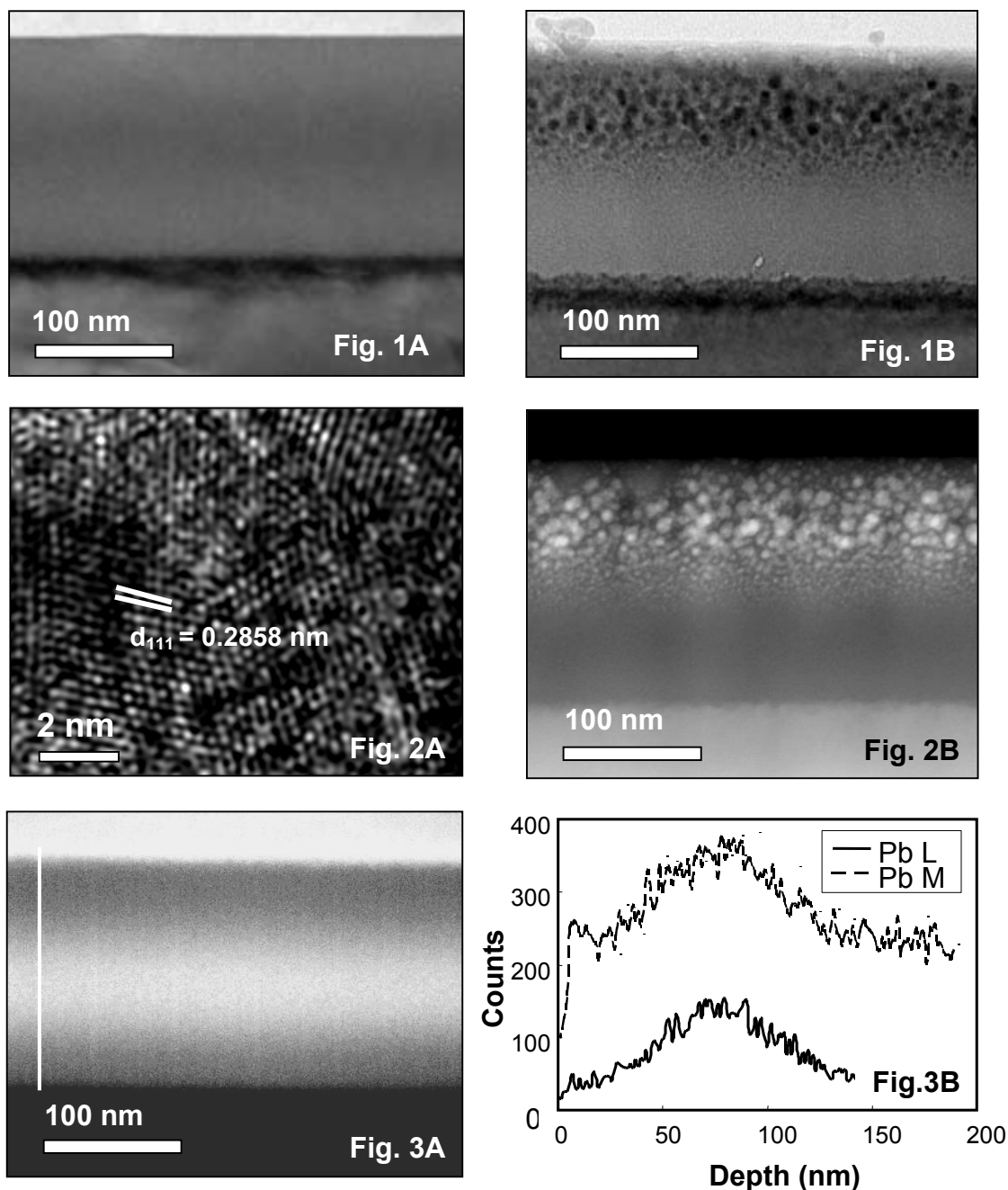


FIG. 1. Cross-sectional TEM images of 300 keV Pb⁺ implanted zircons showing the formation of amorphous layer and nanoparticles at ion fluences: (A) 1×10^{16} and (B) 1×10^{17} ions/cm², respectively.

FIG. 2. High-resolution TEM (A) and HAADF-STEM (B) images showing the formation of Pb nanoparticles (1×10^{17} ions/cm²).

FIG. 3. (A) HAADF-STEM image showing the Pb⁺ elemental distribution in implanted zircon matrix (1×10^{16} ions/cm²); (B) Pb⁺ profile in zircon matrix obtained by STEM-EDS scanning along the white line in Fig. 3A.