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The effect of He and swift heavy ions on nanocrystalline zirconium nitride

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ABSTRACT

Recent studies have shown that swift heavy ion irradiation may significantly modulate hydrogen and helium behaviour in some materials. This phenomenon is of considerable practical interest for ceramics in general and also for candidate materials for use as inert matrix fuel hosts. These materials will accumulate helium via (n, α) reactions and will also be subjected to irradiation by fission fragments. Cross-sectional transmission electron microscopy and scanning electron microscopy was used to study nanocrystalline ZrN irradiated with 30 keV He to fluences between 10^{16} and 5×10^{16} cm^{-2}, 167 MeV Xe to fluences between 5×10^{13} and 10^{14} cm^{-2} and also 695 MeV Bi to a fluence of 1.5×10^{13} cm^{-2}. He/Bi and He/Xe irradiated samples were annealed at temperatures between 600 and 1000 °C and were analysed using SEM, XTEM and selected area diffraction. The results indicated that post irradiation heat treatment induces exfoliation at a depth that corresponds to the end-of-range of 30 keV He ions. SEM and XTEM analysis of He/Xe irradiated samples revealed that electronic excitation effects, due to Xe ions, suppress helium blister formation and consequently the exfoliation processes. He/Bi samples however do not show the same effects. This suggests that nanocrystalline ZrN is prone to the formation of He blisters which may ultimately lead material failure. These effects may however be mitigated by electronic excitation effects from certain SHIs.

1. Introduction

ZrN has been identified as a candidate material for use as an inert matrix fuel host [1]. These materials will host plutonium and minor actinides and also possibly nuclear fuel and will therefore be subject to irradiation by fission fragments and alpha particles [2]. In order to show that these materials are suitable for use as inert matrices the effects of these types of irradiation on the materials must be investigated. The effect of alpha particle irradiation is simulated by means of He implantation and that of fission fragments by the irradiation of the material with swift heavy ions (SHI). Since these materials will experience both types of irradiation it is also important to investigate their combined effects on defect production. He irradiation can lead to the formation of helium bubbles and exfoliation at elevated temperatures. The agglomeration of helium usually results from diffusion and can lead to the formation of blisters or bubbles and exfoliation depending on the material and the implantation depth. Bubble formation, blistering and exfoliation has been observed by various researchers in many different materials such as Si [3,4], nanocrystalline VN [5], TiO_2 [6], nanocrystalline Fe [7], ZrO_2, $MgAl_2O_4$, MgO and Al_2O_3 [8] and in SiC, Si_3N_4, MgO, Al_2O_3, and $MgAl_2O_4$ [9]. However SHIs can possibly mitigate these effects due to their unique interaction with materials. Swift heavy ion induced epitaxial crystallisation (SHIBIEC) has been observed in various materials. This process produces results similar to ion beam induced epitaxial crystallisation (IBIEC) described by Heera et al. [10]. The mechanisms involved are very different IBIEC occurs with ions with energies in the keV range and SHIBIEC with ions with energies >100 MeV. According to Benyagoub et al. [11] SHIBIEC may occur at room temperature (RT) whereas IBIEC usually only occurs at elevated temperatures. SHIBIEC has been observed at RT in Si [12,13,11] and Ge [14].

2. Materials and methods

ZrN layers, with nanocrystalline microstructure (average crystallite size of ~4 nm), with a thickness of 20 µm were produced via vacuum arc-vapour deposition. In essence this process is the condensation of a substance in vacuum, assisted by ion bombardment,

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onto a substrate (in this case silicon). A detailed explanation of the deposition details is provided in [15].

Low energy He implantation was performed at the Facility for Modification and Analysis of Materials with Ion Beams (FAMA) at the Vinča Institute of Nuclear Sciences, Belgrade, Serbia. The implantation was done at room temperature with 30 keV He ions to a fluences between 10^{16} and 5×10^{16} cm^{-2}.

High energy ion irradiation was performed with the U-400 and IC-100 cyclotrons at the FLNR a part of the JINR in Dubna. During irradiation the surface temperature of the target did not exceed 30 °C.

The samples were first irradiated with He ions and subsequently irradiated with 167 MeV Xe and 695 MeV Bi ions, respectively to fluences in the range from 5 × 1013 to 1 × 1014 cm^{-2} for Xe and 1.5×10^{13} cm^{-2} for Bi ions. The surface electronic stopping power according to SRIM 2008 [16] values of Xe and Bi are 30 and 49 keV/nm, respectively.

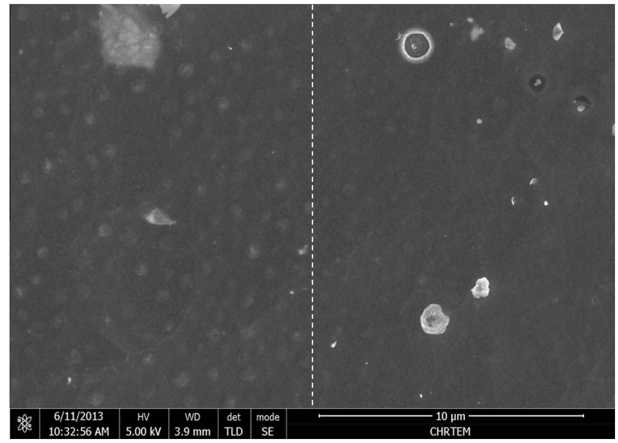

Fig. 2. SEM-SE micrograph of ZrN implanted with 30 keV He to a fluence of 1×10^{16} cm^{-2} and 167 MeV Xe 8×10^{13} cm^{-2} annealed at 700 °C for 30 min. The left hand side is implanted with He only and the right with both He and Xe. The approximate border between the regions is indicated by the superimposed line.

3. Results

Fig. 1(a) shows a SEM micrograph of ZrN implanted with 30 keV He to a fluence of 1×10^{16} cm^{-2} subsequently annealed at 700 °C for 30 min. Small cracks can be seen distributed across the surface of the sample. These cracks are not observed in virgin nc-ZrN samples. The same effect is also seen at higher helium fluences such as 1.5×10^{16} (not shown) and 5×10^{16} cm^{-2} (Fig. 1(b)). The SEM results indicate that the number of helium blisters appears to increase with increasing helium fluence.

Fig. 1(c) shows a SEM micrograph of ZrN implanted with He to a fluence of 1×10^{16} cm^{-2} and also irradiated with 695 MeV Bi ions to a fluence of 1.5×10^{13} cm^{-2} subsequently annealed at 700 °C for 30 min. A large number of blisters can still be seen after Bi irradiation. Similar results were obtained for samples with a higher He fluence (1.5×10^{16} cm^{-2}) and the same Bi fluence (not shown).

Fig. 2 shows a SEM micrograph of ZrN implanted with 30 keV He to a fluence of 1×10^{16} cm^{-2} and 167 MeV Xe 8×10^{13} cm^{-2} subsequently annealed at 700 °C for 30 min. The border between the areas irradiated with He only and He + Xe is indicated on the micrograph. Blisters can clearly be seen on the side which was implanted with He and are only occasionally observed on the side which was irradiated with He and Xe. Both sides of the sample were subjected to the same heat treatment, the only difference being the Xe irradiation. This suggests that the lack of blisters is most likely a consequence of Xe irradiation.

The suppression of blisters at a higher He fluence (5×10^{16} cm^{-2}) by high energy Xe ion irradiation is also evident from Fig. 1(d). The number of blisters in Fig. 1(d) appears to have decreased after Xe irradiation to a fluence of 8×10^{13} cm^{-2}, when compared with Fig. 1(b).

Bright field XTEM micrographs of nc-ZrN implanted with He and Bi are shown in Fig. 3. The samples were implanted with He and Bi to fluences of 1×10^{16} and 1.5×10^{13} cm^{-2}, respectively. Fig.3(a) shows an as-implanted sample before Bi implantation. Fig. 3(a–c) are micrographs from samples which have been annealed at 700, 800 and 900 °C, respectively. All samples were annealed for approximately 30 min.

The TEM and SEM results showed that Bi irradiation does not significantly suppress blister formation. Before annealing TEM analysis does not revealed clear evidence that the sample has been

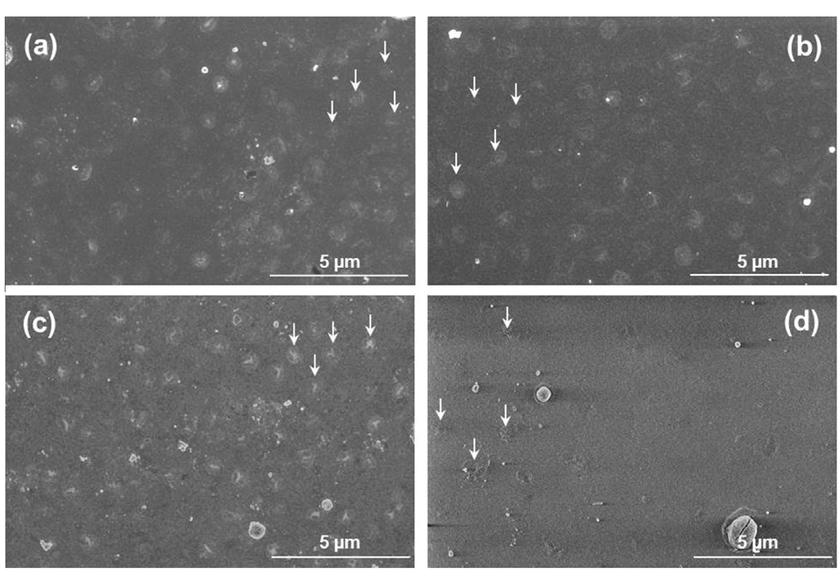

Fig. 1. SEM-SE micrographs of nc-ZrN implanted with 30 keV He to a fluence of (a) 1×10^{16} cm^{-2} and (b) 5×10^{16} cm^{-2} and micrographs of nc-ZrN (c) 1×10^{16} cm^{-2} He and 8×10^{13} cm^{-2} Xe and (d) 5×10^{16} cm^{-2} He and 8×10^{13} cm^{-2} Xe. All were annealed at 700 °C for 30 min. The arrows indicate the location of a number of blisters and also gives some measure of their density.