Establishing control over VO_2 phase transformations through radiation-induced defects

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Background and introduction

Neuromorphic computing aims to emulate and surpass the energy-efficiency of the human brain but requires the design and experimental realization of an altogether new palette of neuron- and synapse-like materials. The metal–insulator transition (MIT) of VO_2 provides a sensitive and versatile vector for achieving the necessary conductance switching required to fashion the neuroemulative circuits necessary to fully realize brain-inspired computing. While the effect of point and planar defects on the transition characteristic of materials with an MIT has been recorded, several knowledge gaps exist.[1,2] In this work, we seek to elucidate the specific defects generated in VO_2 upon α-irradiation and how such defects modify their memristive response.

Methodology

Ge-doped VO_2 particles were prepared hydrothermally at 250°C through reduction of 8 mL 0.4 M vanadic acid by 3 mL isopropanol in the presence of 5—50 mg solid GeO_2 and 5 mL water followed an annealing at 550°C under Ar for 6 h. The as-prepared particles were affixed to either a silicon nitride, or silica glass membrane by drop casting which were then loaded onto an aluminum backing plate. The samples were irradiated by 3 MeV α-particle irradiation using a helium (4He) beam at a constant current under vacuum to avoid oxidation of VO2 to V_2O_5. Target irradiation doses from $9.46*10^{14}$ cm^{-2} to $6.44*10^{15}$ cm^{-2} were achieved by controlling exposure times (1 h – 10.5 h). The dynamical behavior the VO_2 particles was measured before and after irradiation exposure through differential scanning calorimetry (DSC) using a TA Instruments Q2000 instrument. Irradiation effects were imaged by transmission electron microscopy (TEM) using an FEI Tecnai TEM operated at 200 kV.

Results and discussion

Fig. 1 shows the heating and cooling transitions of Ge-doped VO_2 upon cycling at a heating and cooling rate of 10°C/min from 0°C to 100°C for the unirradiated samples (Figs. 1A and 1C) and from 0°C to 150°C for the irradiated samples (Figs. 1B and 1D). Fig. 1B ($9.46*10^{14}$ cm^{-2}) and 1D ($6.44*10^{15}$ cm^{-2}) show that the irradiation effects are manifested as a one-time depression of the heating transition temperature (Cycle 1, Figs. 1B and 1D). A return to the pre-irradiated transition temperature upon heating to 150°C is observed suggesting an annealing phenomenon which 'heals' the aforementioned irradiation damage (Cycle 2, Figs. 1B and 1D). Here, a shift in the cooling transition is not readily apparent. Moreover, the hysteresis width is not lowered which indicates that the effect of the induced damage is not easing the nucleation step of the phase transition in a way that has been previously observed for point defects

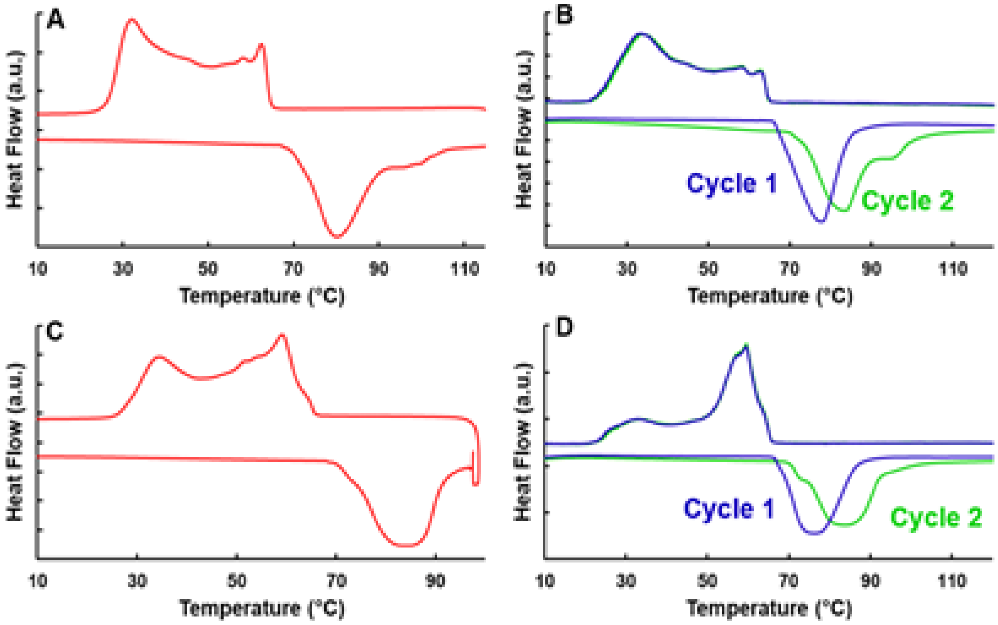

Fig. 1. DSC Cycles of Ge-Doped VO_2. A and C plot the thermograms of two independent Ge VO_2 samples prior to irradiation with alpha particles and B and D plot the same respective samples post irradiation. The Ge-Doped sample in A and B was irradiated with a dose of $9.46*10^{14}$ cm^{-2} over 1 hour and the sample in C and D was irradiated with a dose of $6.44*10^{15}$ cm^{-2} for 10.5 hours. To show the cycling behavior two cycles of the irradiated sample are shown in B and D with the first cycle in blue and the second cycle in green.

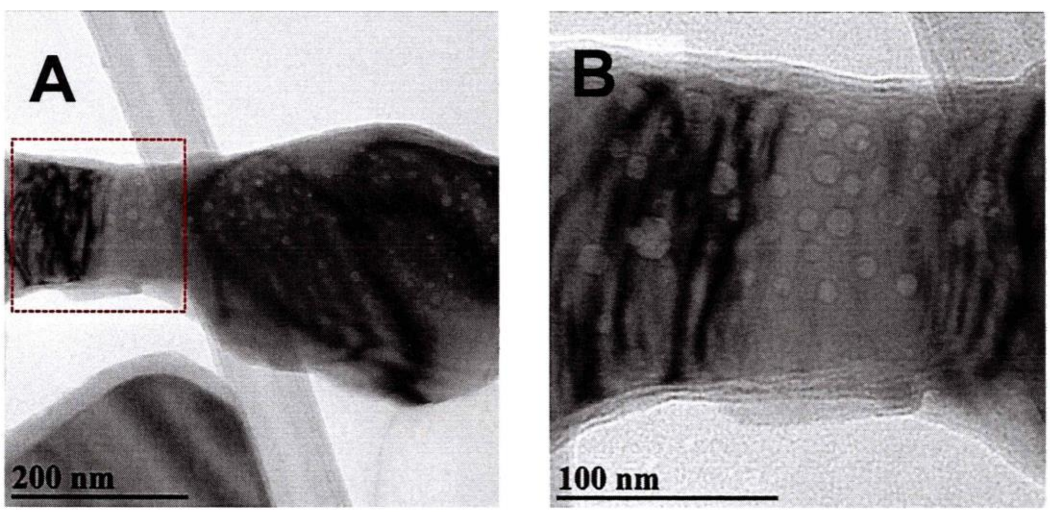

Fig. 2. (A) Voids formed inside of Ge-doped VO_2 nanoparticle after irradiation. (B) Shows a close-up view of the red boxed area in (A)

The TEM images shown in Figs. 2A and 2B reveal the formation of intraparticle voids which are likely caused by He bubble generation, (zoomed-in image of the boxed area (Fig. 2A, red) is shown in Fig. 2B. Here, the facets are most likely related to the crystallography of VO_2, wherein the atoms within the most closely packed planes are preferentially displaced during irradiation. We postulate that the observed resetting of the heating transition temperature may result from a heat-induced evacuation of the observed He.The observations gleaned from DSC and TEM characterization suggest that while the effects of irradiation damage in Ge-doped VO_2 are significant, further experiments are required to elucidate the mechanism of their action on the MIT of this material.

[1] W. Fan, J. Cao, J. Seidel, Y. Gu, J.W. Yim, C. Barrett, K.M. Yu, J. Ji, R. Ramesh, L.Q. Chen and J. Wu, Phys. Rev. B **83**, 235102 (2011).

[2] H. Clarke, B.D. Carraway, D.G. Sellers, E.J. Braham, S. Banerjee, R. Arróyave, and P.J. Shamberger, Phys. Rev. Mater. **2**, 103402 (2018).

[3] S.H. Li, J.T. Li, and W.Z. Han, Materials (Basel) **12** (2019).