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Phase transformation and chemical decomposition of nanocrystalline SnO_2 under heavy ion irradiation

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ABSTRACT

A crystalline-to-crystalline phase transformation, including chemical decomposition, has been observed in SnO_2 nanopowder irradiated by 2.2 GeV ^{197}Au ions. X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM) were used to characterize the transformation from tetragonal SnO_2 ($P4_2/mnm$) to tetragonal SnO ($P4/nmm$), with trace quantities of β-Sn ($I4_1/amd$). At a fluence of approximately 2.0×10^{12} ions/cm^2, diffraction maxima corresponding to SnO became clearly evident and increased in intensity as fluence increased. The proportion of SnO, as determined by Rietveld refinement of XRD data, reached $23.1 \pm 0.8\%$ at the maximum fluence investigated of 2.4×10^{13} ions/cm^2. Raman spectra show high photoluminescence (PL) intensity before and during initial SnO formation, indicating the importance of oxygen vacancies in the transformation process. Small-angle X-ray scattering (SAXS) analysis provided evidence of ion tracks, but no tracks were observed using high-resolution TEM (HRTEM). The transformation likely occurs through a multiple-impact mechanism, based on the accumulation of O vacancies, defect ordering, and partially localized Sn reduction.

1. Introduction

SnO_2 has many applications in materials engineering due to its bulk and surface properties. It finds applications as a transparent conducting oxide, oxidation catalyst, and solid state gas sensor [1]. Under ambient conditions, SnO_2 exhibits the same tetragonal structure as rutile TiO_2 ($P4_2/mnm$). The unit cell parameters are: $a = b = 4.737$ Å and $c = 3.186$ Å; Z = 2 [2]. Each Sn atom is coordinated with six O atoms, forming columns of slightly-distorted, edge-sharing SnO_6 octahedra. Under hydrostatic pressure of 11.8 GPa, the rutile structure transforms into a $CaCl_2$-type structure ($Pnnm$). At higher pressures: pyrite-type ($Pa\bar{3}$), orthorhombic ($Pbca$), and cotunnite-type ($Pnam$) structures can form [3]. The high temperature behavior of SnO_2 has not been well established and reported critical temperatures vary greatly. The melting point has been measured at both 1625 °C [4,5] and 2000 °C [4], while the vaporization point has even larger discrepancies and was measured at 1830 °C [4] and also 2927 °C [6]. Thermal decomposition of SnO_2 (to SnO, O_2, and sometimes Sn) has also been observed at temperatures between 1300 °C and 1500 °C [2,7,8]. This is not consistent with the observation that SnO is unstable above approximately 370 °C and decomposes into Sn and SnO_2 [9], albeit the reaction rate is slow. Such variations in measured critical temperatures and high temperature stability suggest that a multi-phase equilibrium may exist at high temperatures. Thus, some combination of SnO_2 melt and vapor, metallic Sn, and gaseous SnO and O_2 may coexist over a range of temperatures. The effect of ion irradiation on this polymorphism has not been well studied.

High energy (swift) heavy ions interact with a solid by dissipating their energy to the material's electronic subsystem along their path. As an ion passes through the material, the electrons within a

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cylindrical volume around the ion's trajectory are left in a state of extremely high energy density. This energy is transferred to the atomic lattice leading to varying levels and types of damage, depending on the ion species, energy, charge state, velocity, energy deposition rate (or ion stopping power, dE/dx), as well as the material's ability to recover [10]. The processes involved are very complex and are not fully understood as they occur over picosecond to nanosecond timescales within nanometer-sized volumes. Cylindrical damage regions form, which are termed "ion tracks", have dimensions typically on the order of a few nanometers in diameter and several micrometers in length (depending on the ion energy). Materials that generally exhibit high radiation stability, for example CeO_2 [11–13] and ThO_2 [14], show the formation of defects and lattice effects such as swelling and microstrain, but no changes in crystalline structure. Other oxide materials (such as SiO_2 [15], Al_2O_3 [16], and various complex oxides [17–22]) are more susceptible to radiation damage, exhibiting loss of long-range order which in some cases can be attributed to the accumulation of fully amorphous tracks. Some materials have been shown to undergo crystalline-to-crystalline transformations in response to ion irradiation [23–26], such as ZrO_2 and HfO_2 which undergo a monoclinic-to-tetragonal transformation [23]. Evidence of a different type of radiation response has been reported for GeO_2 [27], CeO_2 [11–13,28], Al_2O_3 [29], yttria-stabilized ZrO_2 [30], UO_3 [13], SiO [31], and InO [32], where observation of some or all of the following related effects have been made: preferential disorder on the O sublattice, O ejection from track cores, cation reduction, and metallic inclusion formation within track cores. These oxides share the aforementioned effects with the alkali-halides LiF [33] and CaF_2 [34], which also show preferential disorder on the anion (fluorine) sublattice.

To date, no single theoretical model is able to fully explain all of the structural modifications observed in different materials. According to the thermal-spike model [35], the mechanism for transformation is the thermal transient that occurs as the dense electronic excitation is transferred to the lattice through electron-phonon coupling. This thermal-spike is responsible for the formation of a melt phase along the ion trajectory and inducing a pressure wave that propagates into the surrounding matrix. As energy is quickly dissipated, non-equilibrium states, such as amorphous, high temperature, or high pressure phases may be quenched along the ion's path [23,25,26,36]. The apparent stability of non-equilibrium phases may be due to the nanoscale track dimensions and kinetic limitations on the ordering process during rapid quenching [37]. Due to its success at describing ion-induced processes in a variety of materials, the thermal-spike model has been widely discussed.

The aforementioned energy transfer processes are very complex, occurring on very short timescales and highly non-equilibrium conditions. The thermal-spike model, however, relies on assumptions of thermodynamic equilibrium, using equilibrium critical values for melting and vaporization to determine melt-thresholds and track diameters, while assigning free parameters to fit experimental data [10,38,39]. Introducing the formation and decay of self-trapped excitons to the previously developed theoretical framework has offered an advancement in understanding for some materials [40–42]. The primary role of self-trapped excitons in this context is to localize electronic energy close to the track core by rendering excitons immobile and therefore unable to decrease energy density in the track through outward diffusion. Their subsequent decay within track regions (through defect production) may better account for the high defect concentrations observed in irradiated materials when compared to the thermal-spike mechanism alone. Exciton self-trapping has also been associated with a change in cation charge state [39], a radiation effect that is not well understood but is observed in a variety of oxides.

Due to the potential for SnO_2 in engineering applications, nanoscale modifications to its structure may have significant technological implications. This paper describes a previously unobserved phase transformation involving chemical decomposition under swift heavy ion irradiation of SnO_2 nanopowder. Complementary characterization techniques, including synchrotron XRD, Raman, SAXS, and TEM, have been used to study these structural modifications in detail over a wide fluence regime.

2. Experimental methods

Sn(IV) oxide powder was obtained from Alfa Aesar with a theoretical density of 6.96 g/cm^3 and grain sizes between approximately 10 and 20 nm, as determined by TEM. Sample holders were prepared by drilling sets of 200 μm diameter holes (using electron discharge machining) into 50 μm thick stainless steel foils. The powder was then pressed into these holes using a hydraulic press at a pressure of 20 MPa. This formed sets of cylindrical sample pellets held within the foils, each approximately 200 μm in diameter and 50 μm thick. Each set contained seven samples for redundancy, in the event that pellets were lost or damaged during irradiation, characterization, or transportation. Ten sets of samples were prepared and irradiated with 2.2 GeV ^{197}Au ions (11.1 MeV/u) at room temperature, using the UNILAC linear accelerator at the GSI Helmholtz Centre for Heavy Ion Research, in Darmstadt, Germany. The sample sets were irradiated to 10 different fluences, increasing from 5.0×10^{10} to 4.9×10^{13} ions/cm^2. The flux was kept sufficiently low to avoid sample heating during irradiation, which was on average 4×10^9 ions/cm^2 s. SRIM code [43] simulation indicated a projected ion range of 56.6 μm based on the material's theoretical density. However, because the fabrication of the pressed powders was not followed by sintering, the actual sample density was significantly lower than the ideal value. The range was therefore corrected, as described previously in detail elsewhere [44], using the actual sample density of approximately 60% of the theoretical value. The resulting ion range is approximately 90 μm, confirming the assumption that all incident ions pass completely through the sample thickness. The electronic stopping power, S_e, was determined to have an approximately constant profile through the sample thickness, with an average value of 44.2 keV/nm ± 1.0 keV/nm.

Post-irradiation analysis included the use of synchrotron XRD with high energy X-rays (λ = 0.407 Å) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Data were collected from at least three sample pellets for a given fluence. The measurements were performed in transmission mode using a CCD detector, with an X-ray spot size of 25 μm and an exposure time of 600 s. The diffraction images were integrated with Fit2D software [45]. The resulting diffraction patterns were then quantitatively analyzed using Rietveld refinement conducted with FullProf software [46]. These analyses utilized pseudo-Voigt function models to fit each peak in the diffraction spectra, as well as the background, to obtain information about each phase present at each fluence. Raman measurements were performed in backscattering geometry with two solid-state lasers (λ = 532 nm, 785 nm) and an Olympus microscope with 100× objective. The laser power was limited to 10 mW to avoid sample heating during the 75 s exposure times. Several measurements were taken on each sample pellet. Samples at various fluences were then dispersed onto holey carbon films supported by Cu grids for TEM analysis. HRTEM imaging and selected area diffraction were completed using an FEI Tecnai G2 F20 X-TWIN TEM with the field emission gun operated at 200 keV. SAXS data were gathered in transmission mode from samples irradiated to 5.0×10^{10} ion/cm^2 at the SAXS/WAXS beamline at the Australian Synchrotron, using 11 keV X-rays and