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Amorphization of Ta_2O_5 under swift heavy ion irradiation

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ABSTRACT

Crystalline Ta_2O_5 powder is shown to amorphize under 2.2 GeV ^{197}Au ion irradiation. Synchrotron X-ray diffraction (XRD), Raman spectroscopy, small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM) were used to characterize the structural transition from crystalline to fully-amorphous. Based on Rietveld refinement of XRD data, the initial structure is orthorhombic (*P2mm*) with a very large unit cell ($a = 6.20$, $b = 40.29$, $c = 3.89$ Å; $V = 971.7$ Å^3), ideally containing 22 Ta and 55 O atoms. At a fluence of approximately 3×10^{11} ions/cm^2, a diffuse amorphous background becomes evident, increasing in intensity relative to diffraction maxima until full amorphization is achieved at approximately 3×10^{12} ions/cm^2. An anisotropic distortion of the orthorhombic structure occurred during the amorphization process, with an approximately constant unit cell volume. The amorphous phase fraction as a function of fluence was determined, yielding a trend that is consistent with a direct-impact model for amorphization. SAXS and TEM data indicate that ion tracks exhibit a core-shell morphology. Raman data show that the amorphous phase is comprised of TaO_6 and TaO_5 coordination-polyhedra in contrast to the TaO_6 and TaO_7 units that exist in crystalline Ta_2O_5. Analysis of Raman data shows that oxygen-deficiency increases with fluence, indicating a loss of oxygen that leads to an estimated final stoichiometry of $Ta_2O_{4.2}$ at a fluence of 1×10^{13} ions/cm^2.

1. Introduction

Ta_2O_5 is a complex and versatile material that has many applications in materials engineering. One of the most notable characteristics of Ta_2O_5 is its high dielectric constant (relative permittivity) [1–11], which has an unusually high value in the range of 25–100 depending on processing factors such as synthesis methodology and annealing temperature [1]. Although the crystalline state has a higher absolute dielectric constant than the amorphous phase (ranging from 56 to 59) [12], it is highly anisotropic. Therefore, the amorphous form is often used in microelectronics in order to avoid this effect [7]. The amorphous form also exhibits improved leakage current properties due to the decreased loss at grain boundaries [13]. The high dielectric constant, high dielectric breakdown strength [2], and good leakage current properties [2,14] make Ta_2O_5 a useful material for gate dielectrics in transistors [1,6], dielectric resonators in microwave communication devices [1], and charge capacitors in dynamic RAM devices [5]. Due to these properties, Ta_2O_5 is also regarded as one of the best candidate materials to replace conventional SiO_2 and Si_3N_4 thin-film circuit devices [12]. This is because Si containing materials have reached their physical limit for size reduction [12] and use of Ta_2O_5 will allow the down-scaling that future microelectronic devices will rely on [4].

Tantalum pentoxide is also widely used due to its optical properties, typically in the amorphous state, in order to avoid scattering loss at grain boundaries [7]. Ta_2O_5 is commonly used as a coating on solar cells due to its high refractive index, forming a low loss, *anti*-reflective layer that increases cell efficiency [1,5,7,8,15]. This material is used in optical waveguides [6], electroluminescent dis-

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plays [6], and also as a photocatalyst [8,15,16]. In addition, it is utilized as a chemical catalyst [7], gas sensor [5,15], proton conductor [7], and in surface acoustic wave devices [6]. As the structure highly affects its usefulness, the crystalline-to-amorphous transition is of great interest.

The structures of various polymorphs are not well defined for Ta_2O_5, largely due to the complexity of their crystallization behavior. There are two common ambient pressure structures, the low temperature L-Ta_2O_5 (or β-Ta_2O_5) phase and high temperature H-Ta_2O_5 (or α-Ta_2O_5) phase. L-Ta_2O_5 is generally considered to be orthorhombic [17–20], comprised of corner- and edge-sharing TaO_6 octahedra and TaO_7 pentagonal bipyramids [21]. A monoclinic model has also been proposed [17]. Although many unit cell parameters have been reported, the value of the longest parameter varies greatly, ranging from approximately 3.66 Å [22] to over 69.55 Å [17] in order to obtain cell symmetry. One of the most widely accepted models, given by Stephenson & Roth [20], is orthorhombic (*P2mm*) with dimensions: $a = 6.20$, $b = 40.29$, $c = 3.89$ Å. This model contains 11 formula units and relies on several O-vacancies and/or Ta-interstitials for charge neutrality; a representation of this structure is shown in Fig. 1.

A hexagonal structure, δ-Ta_2O_5 [23,24], has also been reported and is thought to be stable at ambient conditions along with L-Ta_2O_5. This phase has been shown to have tantalum coordination numbers of both 6 and 8 [25], which has been confirmed by computational simulations of the structure [26]. Transformation of δ-Ta_2O_5 into an orthorhombic structure occurs upon heating to 900 °C [23]. At temperatures above ~1340 °C, L-Ta_2O_5 transforms to H-Ta_2O_5 [5,19]. This structure is often considered to be orthorhombic [27,28], though it apparently has several variants including tetragonal [22,28,29], monoclinic [1,21,22,30], and triclinic [22]. Because the transformation from H-Ta_2O_5 is slow, and cooling of H-Ta_2O_5 has been shown to form several intermediate phases [19], it is difficult to prepare high quality L-Ta_2O_5 crystals by conventional high-temperature methods.

Two main high-pressure phases have been reported, both with monoclinic structures. B-Ta_2O_5 is comprised of TaO_6 polyhedra only [31]; whereas, Z-Ta_2O_5 consists of TaO_7 polyhedra only [24,31]. These two structures are closely related, easily transforming from one to the other, and a mixture of the two structures has been shown to form at 8 GPa and 1197 °C [31]. Another monoclinic phase has been shown to form at 297–347 °C and 20 MPa, denoted ε-Ta_2O_5 [24], which is 6-coordinated and is likely equivalent to B-Ta_2O_5. This ε-Ta_2O_5 phase has been shown to irreversibly transform into L-Ta_2O_5 at 887 °C [24]. Transformation from a monoclinic to trigonal structure has also been observed by very slow cooling from 1000 °C [32].

Materials subjected to swift heavy ion irradiation undergo complex structural modifications at the nano-scale; the extent of modification is dependent on the material as well as the ion species and energy. The effects on relatively radiation-resistant materials consist of defect production and clustering, grain growth, fragmentation, swelling, and polygonization [33,34]. In materials with a higher susceptibility to damage accumulation, the effects include crystalline-to-crystalline phase transformations (often into high temperature or high pressure phases) [35–38], amorphization [2,36,39–43], and cation reduction with associated anion loss [44–48]. Because the properties of a material are so highly dependent on structure, nano-scale structure modifications using ion beams are of great interest.

Swift heavy ions are highly charged heavy atoms accelerated to energies of over 1 MeV/nucleon (often in the GeV range). As the ions bombard a target material, their energy is deposited into the material's electronic subsystem, causing intense electronic excitation and ionization as the ions slow. This energy deposition (ion energy loss, represented by dE/dx) is concentrated in a very small cylindrical volume, with radii of a few nanometers around the ion's trajectory, resulting in extremely high energy densities. The subsequent transfer of energy to the atomic lattice induces a cylindrical damage zone, termed an "ion track". Although there have been many models proposed, there exists no single theory that describes all aspects of ion track formation. According to the thermal-spike model, energy from the electronic subsystem is transferred to atoms within the lattice through electron-phonon coupling, causing a sharp increase in temperature throughout the ion track [49–52]. This high-temperature transient results in the melting or vaporization of material within this region, leaving behind a highly modified and defective structure (often amorphous) after rapid quenching to the bulk. This model also provides a framework for understanding the high-temperature and high-pressure phase formation during irradiation, as rapid kinetics may lead to crystallization of these structures during the transient. The Coulomb-explosion model provides an alternative model for track formation, and focuses on the massive charge separation caused by dense ionization, inducing strong electro-static forces that displace atoms from their sites [53–55]. Alternative models have also been proposed, that describe damage formation based on the decay of self-trapped excitons [56,57] and bond-weakening [58,59].

Ion tracks are typically on the order of several nanometers in diameter and many microns in length. This geometry is unique to swift heavy ion effects. Due to the significance of Ta_2O_5 in engineering applications, nanoscale modifications to its structure may have significant technological implications. This paper describes the first swift heavy ion irradiation study of crystalline Ta_2O_5, which leads to amorphization along the ion tracks. Synchrotron-XRD data were obtained for detailed structural characterization over a wide fluence regime, Raman spectroscopy for details on short-range order modifications, along with SAXS and TEM analyses for ion track and grain morphology characterization.

2. Experimental methods

Tantalum(V) oxide powder was obtained from MTI Corporation with a theoretical density of 8.2 g/cm^3 and particle sizes on

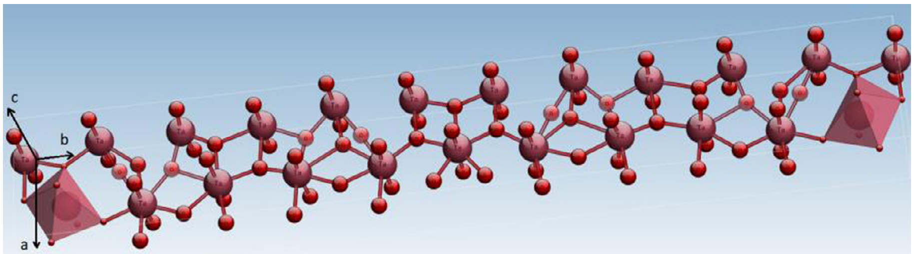

Fig. 1. Orthorhombic structure model proposed by Stephenson & Roth [20], comprised of TaO_6 and TaO_7 polyhedra.