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Formation of solid thorium monoxide at near-ambient conditions as observed by neutron reflectometry and interpreted by screened hybrid functional calculations

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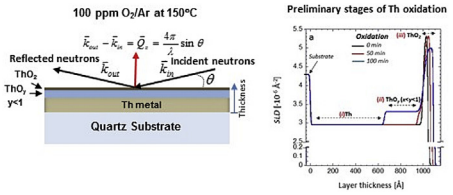
HIGHLIGHTS

- The long-sought solid form of thorium monoxide forms as thin-film thorium oxidizes.
- Density-functional calculations suggest that ThO forms for kinetic reasons.
- A pathway to producing ThO as a majority phase for future studies is now open.
- Dynamic, in-situ neutron reflectometry is valuable for studying oxidation.
- At low oxygen content in the lattice octahedral sites are preferred.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxidation of a ~1000 Å sputter-deposited thorium thin film at 150 °C in 100 ppm of flowing oxygen in argon produces the long-sought solid form of thorium monoxide. Changes in the scattering length density (SLD) distribution in the film over the 700-min experiment measured by in-situ, dynamic neutron reflectometry (NR) shows the densities, compositions and thickness of the various thorium oxides layers formed. Screened, hybrid density-functional theory calculations of potential thorium oxides aid interpretation, providing atomic-level picture and energetics for understanding oxygen migration. NR provided evidence of the formation of substoichiometric thorium oxide, ThO_y ($y < 1$) at the interface between the unreacted thorium metal and its dioxide overcoat which grows inward, consuming the thorium at a rate of 2.1 Å/min while y increases until reaching 1:1 oxygen-to-thorium. Its presence

Abbreviations: SLD, Scattering length density; NR, neutron reflectivity; ppm, parts per million; fcc, face-centered cubic; eV, electron-volt; χ^2, chi-squared; TOF, time-of-flight; SPEAR, Surface Profile Analysis Reflectometer; VASP, Vienna Ab-initio Simulation Package; HSE, Heyd-Scuseria-Ernzerhof; DFT, Density Functional Theory.

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DFT

indicates that kinetically-favored solid-phase ThO can be preferentially generated as a majority phase under the thermodynamically-favored ThO_2 top layer at conditions close to ambient.

1. Introduction

Thorium is one of only two actinides with commercial applications independent of its radioactive nature. Thorium is used to impart high strength and creep resistance in magnesium alloys [1,2]. It also has utility as an oxide as a catalyst [3] and in high-quality lenses for cameras and scientific instruments [4]. The phase diagram for thorium and oxygen shows that only one oxide phase is thermodynamically present at ambient pressure: thorium dioxide [5]. ThO_2 has one of the highest melting point (3300 °C) of all oxides [6] and thus used in heat-resistant ceramics [3] and in mantles of portable gas lights. The availability of 5f orbitals diffuse enough to be involved in molecular bonding enables unusual chemical compounds [7]. Thorium atoms can also bond to more atoms at one time than any other element. For instance, in the compound thorium aminodiboranate, thorium has a coordination number of fifteen [7].

The most important future application of thorium may be as an advanced nuclear fuel. Thorium (^{232}Th) is not itself fissile and so is not the fissile fuel in a thermal neutron reactor. However, it is 'fertile' and upon absorbing a neutron will transmute to ^{233}U, which is an excellent fissile fuel and has considerable advantages including safety and proliferation resistance [8,9]. Current research in nuclear power generation is aimed at reduction of Pu and minor actinides in the spent light water reactor's fuel stockpiles [10]. Considerable research is underway to evaluate the suitability of Th as a nuclear fuel. However, both simplest forms considered-the metal or the dioxide—have significant disadvantages [11]. For example, because thoria's inertness, it is difficult to dissolve spent ThO_2-based fuels in nitric acid [8]. Therefore, production and characterization of new thorium-based materials for nuclear fuels is of great importance.

Could a metastable, solid ThO be such a material? The gas-phase, diatomic molecule, ThO, is long known [12]. It can be formed during the vaporization of ThO_2 [13]. Recently, ThO has been produced through laser ablation of Th metal in the presence of oxygen [14–16] and has been characterized in both the gas phase and in a cryogenic matrix [14,17]. It is being studied in the search for a permanent electron electric dipole moment (eEDM), an important fundamental modern physics problem [18,19]. Interestingly, recent theoretical work suggests that solid ThO is stable under high-pressure conditions [20]. Nevertheless, the clear demonstration of solid ThO as a dominant phase at ambient conditions has not been observed, though it has been long-sought [21,22].

Evidence for the production under mild heating of relatively stable, solid-phase ThO is here demonstrated. It is further shown that ThO can constitute the largest volume of the thorium oxide phases present. The detection method is neutron reflectometry (NR). NR is known as a noncontact, nondestructive, Å-resolution analytical technique for characterizing chemical speciation of thin films, including nuclear materials [23]. This paper also describes how the NR method was extended as a time-resolved (i.e., dynamic), in situ tool to identify the presence, stoichiometry and growth rate of subsurface layers under controlled oxidation conditions. Specifically, NR was employed to understand the oxidation of thorium in ~100 ppm of oxygen at 150 °C. Both the growth rate of the ThO_2 surface layer and of a substoichiometric ThO_w ($w \leq 1$) layer formed between the ThO_2 top layer and the unreacted thorium metal beneath it were measured. To aid in interpretation of the experimental observations screened hybrid-functional calculations were performed on various hypothetical thorium-oxygen structures. This work, also reported herein, provides evidence that a stable ThO layer can formed for kinetic, rather than, thermodynamic reasons.

2. Experimental and computational methodologies

2.1. Thorium thin-film deposition

A nominal 1000 Å thick thorium film was deposited on a ~7.62-cm diameter, 1-cm thick crystalline quartz substrate for the neutron reflectometry experiments by DC-magnetron sputtering. Special care was taken to achieve low impurity content and small thickness variation in the sputtered film.

Prior to the deposition the cryopumped, high-vacuum deposition chamber achieved a base pressure $<2 \times 10^{-4}$ Pa as determined by an ion gauge. The sputter working gas was high purity argon. System pressure could be set by adjusting its flow rate. The system pressure during sputtering was a compromise to achieve stable plasma which requires higher pressure and increasing the mean free path of the sputtered atoms by lowering the pressure. Low pressure promotes good film adhesion to the substrate and high film density. The pressure was adjusted to be ~0.35 Pa as determined using a "0.1 torr" Baratron (capacitance manometer). In the DC- magnetron sputtering system, a Meivac MAK sputter source with a 10-cm diameter thorium target (raw material from Nuclear Fuel Services) was used in the "sputter-up" configuration. The target-to-substrate distance was adjustable from about −2 cm (that is, the target could be adjusted to be above the level of the substrate) to 15 cm. Prior to film deposition the thorium target was sputtered in the −2 cm position to prevent sputtered atoms from reacting the surface of the substrate. This presputtering for ~5–7 min removes the native oxide layer and ensures that the thorium deposited on the substrate is as oxygen-free as possible. Prior studies had shown that no atoms are deposited during this cleaning operation. Since the native thorium oxide is an insulator its removal from the surface of the target can be therefore detected as the gradual decrease and plateauing of the magnitude of the target voltage.

Thickness uniformity and surface smoothness are essential for the NR measurements. Three factors contributed to thickness uniformity. First, a planetary system was employed. That is, the substrate was spun around its central axis as the sample tray was slowly rotated over the target at 15°/s for 20 revolutions. In addition, a large substrate-target distance (10 cm) was chosen. Lastly, a large target was employed. For the same target-substrate distance, sputtering from a large target is inherently capable of producing better uniformity. This is because the atoms emerge from a distributed source. Due to the distribution of the magnetic field behind the target in the MAK sputter gun most of the sputtered atoms emerge from a circular race track about 6 cm in diameter on the surface of the thorium target. The magnets confine electrons in