Key Issues Review

Advances in actinide thin films: synthesis, properties, and future directions

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Abstract

Actinide-based compounds exhibit unique physics due to the presence of 5f electrons, and serve in many cases as important technological materials. Targeted thin film synthesis of actinide materials has been successful in generating high-purity specimens in which to study individual physical phenomena. These films have enabled the study of the unique electron configuration, strong mass renormalization, and nuclear decay in actinide metals and compounds. The growth of these films, as well as their thermophysical, magnetic, and topological properties, have been studied in a range of chemistries, albeit far fewer than most classes of thin film systems. This relative scarcity is the result of limited source material availability and safety constraints associated with the handling of radioactive materials. Here, we review recent work on the synthesis and characterization of actinide-based thin films in detail, describing both synthesis methods and modeling techniques for these materials. We review reports on pyrometallurgical, solution-based, and vapor deposition methods. We highlight the current state-of-the-art in order to construct a path forward to higher quality actinide thin films and heterostructure devices.

Keywords: strong correlations, 5f-electrons, molecular beam epitaxy, actinides

(Some figures may appear in colour only in the online journal)

1. Introduction

Due to their strong electronic correlations and populations of dual-natured 5f electrons, the actinide elements, with atomic numbers ranging from 89 to 103, represent a rather poorly understood section of the periodic table. These transition elements with partially filled 5f electronic subshells exhibit a wide range of exotic properties. The unique characteristics of the actinides’ electronic structure arise from the presence of f-electron orbitals, which due to their high directionality and limited spatial extent give rise to different bonding behaviors. Their 5f electrons can participate in bonding
(leading to itinerant 5f-states), or they offer little or no cohesion leading to 5f-electron localization [1]. The former is characteristic of light actinides (Th–Np) and the latter is characteristic of heavy actinide elements (Am–Cf). The transition between these trends is sometimes called the Mott transition in the actinide series, marking the uniqueness of the Pu element [2]. Actinides also have multiple oxidation states: in an aqueous solution, Pu can exist in four different states simultaneously, for example. They also exhibit divergent magnetic properties, from nearly magnetic (Np and Pu) to transition-metal-like behavior (Th, Pa, U) [3]. The interaction between elements and compounds containing these f electrons is complex enough to give rise to the formation of narrow energy bands and give rise to effects such as long-range magnetic order, Kondo effect, heavy-fermion ground state, valence fluctuations, and/or unconventional superconductivity have been observed (for a review, see, e.g., [4, 5]). Technologically, the most widely used actinide compound to date has been UO₂, in its role as the primary fuel for commercial nuclear energy production [6, 7].

Despite these unique physical properties, their scarcity, inherent radioactivity, and challenges concerning their synthesis mean that actinide materials are still some of the least understood elements. Transuranic actinides and their compounds have been confined to specialized facilities where materials control and accountability can be ensured. Their study and understanding are further hindered by their low natural abundance and typically short half-lives, which limit material supply [1]. Developing an understanding of the fundamental properties and performance characteristics of actinide compounds is hence a challenging but highly active area of research [8]. Understanding the physics of these complex materials more deeply will ensure their continued technological relevance, and open new avenues for discovery in the domains of quantum science and strongly correlated systems.

One way to enable this expansion in our understanding is to minimize the structural complexity in experimental specimens. In practice, this could include removing crystallographic defects, grain boundaries, chemical heterogeneities, and other imperfections during the synthesis process. To this end, thin film synthesis techniques have been used to produce high-quality, single crystalline specimens of various actinide compounds, including those used in nuclear fuel, to study their physical properties [9]. Such efforts also aid comparison between experimental measurements and results from modeling and simulation tools. The geometries of these thin-film samples also permit the implementation of 'microlaboratory' experimental designs, wherein chemical reactions may be explored in detail [10]. It is important to note that due to their scarcity, reactivity, radioactivity, and toxicity, high-purity actinide samples in any geometry have only recently become available to use as targets or sources [11]. Key studies on the technological applications of specific actinides have been summarized in review articles and books, highlighting the remaining problems and advances in research over the years [12]. However, despite these constraints, researchers have found ways to explore a range of physical, chemical, and solution-based techniques capable of producing actinide-based films with varying degrees of success and quality. Here we catalog the successes, and highlight some of the unique property and performance data generated to date.

This review is organized as follows: in section 2 we describe the synthesis methods used to create actinide-based thin films. Section 3 provides a review of actinide thin films that have been successfully synthesized, along with the techniques used for their structural, electronic, and surface characterization. Section 4 summarizes the current and theorized properties of actinide thin films, and in section 5 we give an overview of the efforts and challenges related to modeling these structures. Finally, in section 6 we explore the rich scientific and technological promise of combining different actinide thin films into heterostructures, together with the associated challenges for this next step in the use of these important compounds.

2. Synthesis methods

Ever since the discovery of radiation and its properties, there has been a need to refine and purify actinide materials. During the twentieth century, the focus shifted from Ra to U in the more than 180 minerals containing these elements [13]. Motivated by the applications of radioactive compounds, technology evolved and reports began to emerge of the synthesis of actinide single crystals and thin films. One of the earliest examples is from 1955, when Pu and U were dissolved in a cellulose lacquer and painted on metallic foils [14]. The intervening 70 years have seen synthesis techniques developed that incorporate the refined safety measures necessary to handle these materials.

Spirlet and Voigt summarized the first attempts at refining actinide metals and compounds [11]. Their review article includes the metallothermic reduction of oxides and halides, as well as vacuum melting, selective evaporation and condensation, electorefining, zone melting, and electrotransport (see [11] and references therein). They highlight solution-based techniques as the most economical approach for single crystal synthesis, albeit not directly focused toward thin films. In the 40 years since Spirlet and Voigt’s review, growth of high quality single crystal actinides has advanced enormously, and these samples are of increasing interest from a fundamental scientific perspective. As safety standards evolve and more institutions have access to actinide sources, here we discuss the different approaches that will be instrumental in helping single-crystal actinides reach their full potential. Figure 1 summarizes several of these techniques including pyrometallurgical, solution-based, and different chemical, physical, and pulsed vapor deposition techniques. Table 1 also lists
2.1. Pyrometallurgical methods

In early attempts to fabricate bulk single crystals, actinide compounds such as oxides or alloys were placed in crucibles. When subjected to extreme temperatures and pressures, the required materials are evaporated from the solid source onto a substrate (figure 1(a)). The high melting points and chemical activity of actinide and rare-earth materials used in this early attempt presented a challenge for substrate and crucible material selection. Among the first reports attempting to grow actinide thin films was mineralization. In this approach, a crucible is placed on a rotating, water-cooled support, connected to a direct current (DC) power supply. A tungsten wire acts as a cathode, emitting electrons that weld a lid onto the crucible. Then, by heating the crucible very close to its melting temperature, single crystals can grow inside from the source material over a period of weeks [3, 11, 15]. In this way, Ac₂O₃ was chemically converted to a face-centered cubic (fcc) Ac metal powder, along with the presence of actinium hydride discovered through x-ray diffraction (XRD) [16]. Similar approaches have yielded samples of Th₃N₄ [17], UN [18], U₂N₃ [18], USb [15], UTe [15], and U metal [19]. Different transuranic elements can be synthesized into thin films by reducing their oxide compounds. These materials are loaded into a Ta crucible, together with a reducing agent. The crucible is then heated with DC filaments in order to evaporate the pure metal and condense it onto a cooler substrate outside of the crucible [19]. Pyrolytic decomposition has been used to thermally break down precursor molecules containing U and Am, and form thin films of these active species [20]. In general, these early methods introduced large numbers of impurities, and resulted in poor control over the crystal quality of each sample. Nonetheless they helped researchers improve their understanding of growth parameters and physical properties, paving the way for more innovative approaches.

2.2. Solution-based methods

The levels of radioactivity in some actinide materials make it impractical to handle of more than trace amounts in facilities not designed for this purpose. Dissolving these trace amounts in solution helps minimize the amount of radioactive elements involved in single-crystal growth (figure 2(b)). One of the most successful approaches to solution deposition to date is polymer assisted deposition (PAD), where precursor molecules are made by binding the metal ions of interest to a polymer. As this polymer solution evaporates, the metal film grows. This technique allows researchers to bypass the need for vacuum equipment by controlling the growth process through the viscosity and homogeneity of the metal-bearing precursor polymers [21–24]. Electrodeposition is another solution-based approach. Atoms of the required metal are suspended in solution and mixed with a metallic stirrer that acts as the anode, while a suitable metal plate onto the substrate serves as the cathode.
Table 1. Actinide single crystal and thin film synthesis summary.

| Compound | Growth method | Buffer layer(s)—substrate | Reference |
|----------|---------------|-----------------------------|-----------|
| Ac/AcH₂  | Solid reaction| N/A                         | [16]      |
| Pa       | Solution      | Zn, Al, Mn                  | [1]       |
| ThO₂     | RF sputtering | Various                     | [48]      |
|          | RF sputtering | Glass/Si                    | [49]      |
|          | Photochemical deposition | Polyimide membrane | [32] |
|          | EBE           | Poly-Ir                     | [50]      |
|          | Hydrothermal  | N/A                         | [33]      |
| ThN      | Metal reaction| N/A                         | [17]      |
| Th₃N₄   | DC sputtering | Si(111)                     | [52]      |
|          | Reactive sputtering | Poly-Ta foil               |           |
|          | DC magnetron sputtering | (011)_{CaF₂}∥(1102)_{Al₂O₃} | [53]      |
|          | Reactive sputtering | Spectrosil quartz glass    | [77]      |
|          | DC sputtering | Quartz glass                | [78]      |
|          | Cathode sputtering | Niobium                    | [79]      |
|          | Nitridation   | N/A                         | [18]      |
| ThN₅    | DC sputtering | Si(111)                     | [54]      |
|          | Reactive sputtering | Glass                    |           |
|          | DC magnetron sputtering | (111)_{UN₅}∥(001)_{LAO}   | [23]      |
|          | Reactive sputtering | LAO(001)/CaF₂(100)        | [82]      |
|          | Reactive magnetron sputtering | r-Al₂O₃          | [83]      |
|          | Reactive magnetron sputtering | YSZ(001)      | [83]      |
|          | Reactive sputtering | (001)_{YZO}∥(011)_{LAO}  | [61, 84] |
|          | Magnetron sputtering | (001)_{UO₂}∥(001)_{YSZ} | [85]      |
| U₂N₅    | Cathode sputtering | Si(100)                   | [81]      |
|         | Nitridation     | N/A                         | [18]      |
|         | Si(111)         | Poly-Ta foil                |           |
| UN₂     | Reactive sputtering | CaF₂                      | [53]      |
| UO₂     | PAD            | (111)_{UO₂}∥(001)_{LAO}   | [22, 23] |
|         | Reactive sputtering | LAO(001)/CaF₂(100)        | [82]      |
|         | Reactive magnetron sputtering | r-Al₂O₃          | [83]      |
|         | Reactive magnetron sputtering | YSZ(001)      | [83]      |
| U₃O₈ (cmmm) | PAD            | (001)_{UO₂}∥(001)_{YSZ}  | [62]      |
|          | Magnetic sputtering | (111)_{UO₂}∥(011)_{Si}  | [85]      |
|         | Sputtering      | Mo                          | [86]      |
|         | CVD            | UO₂ on Si                   | [36]      |
|         | PLD            | (100)_{YO₂}∥(110)_{LAO}   | [6]       |
|         | PAD            | (001)_{YO₂}∥(001)_{LAO}   | [22, 23] |
|         | Sol–gel        | MgO                         | [87]      |
|         | Sol–gel        | Al₂O₃                       | [87]      |
|         | Solution/foil  | Fe                          | [28]      |
|         | Solution spin coat | Al                 | [34]      |
|         | DC sputtering  | (001)_{YO₂}∥(011)_{SrTiO₃} | [63]      |
|         | DC sputtering  | (111)_{YO₂}∥(111)_{YSZ}   | [64]      |
|         | Hydrothermal   | CaF₂                        | [30, 31] |
|         | Hydrothermal   | CaF₂, ThO₂, UO₂, YSZ      | [8]       |
|         | CVD            | Si                          | [35]      |
|         | Reactive magnetron sputtering | TiO₂, Al₂O₃, YSZ, ZnO, NdGaO₃ | [60]      |
|         | PAD            | Si                          | [65]      |
|         | Spin coat combustion | Al sheet                | [66]      |
| U–O–Pd  | Sputter co-deposition | Si                 | [88]      |
| U₅O₈ (P62m)| PAD            | Al₂O₃(001)                 | [23]      |
|         | Reactive magnetron sputtering | r-Al₂O₃          | [83]      |
| U₃O₈ (cmcm)| PAD            | Al₂O₃(012)                 | [23]      |
| α–UO₃   | PAD            | LSAT(100)                  | [21]      |
| α–U₁O₈  | PAD            | LSAT(100)                  | [21]      |
| UC₃O₇  | Reactive DC sputtering | Si(111)               | [58]      |

(continued on next page)
| Compound | Growth method | Buffer layer(s)—substrate | Reference |
|----------|---------------|---------------------------|-----------|
| UO<sub>3</sub>N<sub>y</sub> | Reactive DC sputtering | Si(111) | [58] |
| U<sub>1-x</sub>Mo<sub>x</sub> | DC magnetron sputtering | Nb(110)/Al<sub>2</sub>O<sub>3</sub>(1110) | [90] |
| UMo | DC magnetron sputtering | Nb(110)/Al<sub>2</sub>O<sub>3</sub>(1110) | [57] |
| USb | Mineralization | N/A | [15] |
| UTe | Mineralization | N/A | [15] |
| UC<sub>2</sub> | PAD | (001)_{UC2}(1102) \parallel (011)_{YSZ} | [23] |
| UPt<sub>3</sub> | Sputtering | Al<sub>2</sub>O<sub>3</sub>(1012), LAO(111), SrTiO<sub>3</sub>(111) | [91] |
| U | Diode sputtering | Poly-Al and Mg | [56] |
| Oxide reduction | La crucible | [19] |
| UHV magnetron sputtering | (001)_{U}(011)_{NeW}(1102)_{Al2O3} | [92, 93] |
| UH<sub>2</sub> | Reactive sputtering | Si(001) | [94] |
| U<sub>1</sub>Ti<sub>1-x</sub>O<sub>2</sub> | DC sputtering | Si(111) | [67] |
| (U,Pu<sub>1-x</sub>)O<sub>2</sub> | DC sputtering | Si(111) | [67] |
| UPd<sub>2</sub>Ni<sub>3</sub> | MBE | a- and r-Al<sub>2</sub>O<sub>3</sub> | [37] |
| UNi<sub>2</sub>Al<sub>3</sub> | MBE | a-Al<sub>2</sub>O<sub>3</sub> | [39] |
| UNi<sub>2</sub>Al<sub>3</sub> | MBE | MgAl<sub>2</sub>O<sub>4</sub> | [39] |
| UNi<sub>2</sub>Al<sub>3</sub> | MBE | LaAlO<sub>3</sub>(111) | [38] |
| UNi<sub>2</sub>Al<sub>3</sub> | MBE | (112)_{UNi2Al3}(010)<sub>YAO3</sub> | [39] |
| NpH<sub>2</sub> | Solid–gas reaction | N/A | [95] |
| NpSb | Mineralization | N/A | [15] |
| NpTe | Mineralization | N/A | [15] |
| NpO<sub>2</sub> | PAD | UO<sub>2</sub>/LAO(001) | [23] |
| PAD | YSZ(100) | [23, 24] |
| DC sputtering | Si(111) | [67] |
| NpS | Mineralization | N/A | [75] |
| PuN | Reactive sputtering | Si(111) | [96] |
| PuH<sub>2</sub>/PuD<sub>2</sub> | Solid–gas reaction | N/A | [97] |
| PuSb | Mineralization | N/A | [3, 75] |
| PuAs | Mineralization | N/A | [3] |
| PuBi | Mineralization | N/A | [3] |
| PuCoGa<sub>5</sub> | Flux growth | Not specified | [98] |
| PuSb | Mineralization | N/A | [15] |
| PuTe | Mineralization | N/A | [15] |
| PuO<sub>2</sub> | DC sputtering | Si(111) | [99] |
| PAD | YSZ(100) | [23, 24, 70] |
| Sputtering | α-Pu | [71] |
| α-Pu<sub>2</sub>O<sub>3</sub> | Sputtering | α-Pu | [71] |
| PuSi<sub>x</sub> | DC sputtering | Mo(100) | [76] |
| Am | DC sputtering | Mo(100) | [100] |
| AmN | DC sputtering | Mo(100) | [100] |
| AmO<sub>3</sub> | DC sputtering | Mo(100) | [100] |
| AmO<sub>2</sub> | DC sputtering | Mo(100) | [100] |
| AmSb | DC sputtering | Mo(100) | [100] |
| Am<sub>2</sub> | Solid–gas reaction | N/A | [101] |
| Am | Oxide reduction | La crucible | [19] |
| CmH<sub>2</sub> | Solid–gas reaction | N/A | [102] |
| Cm | Oxide reduction | La crucible | [19] |
| Bk | Oxide reduction | La crucible | [19] |
| Cf | Oxide reduction | La crucible | [19] |
which the film will grow is kept near the cathode [25–27]. This approach has provided an opportunity to study the oxidation states in uranium oxides [22], and to grow thin films of uranium oxides on foils [28].

Other solution-based approaches include hydrothermal synthesis, in use since 1839 when the first barium and strontium carbonate crystals were formed [29]. Pressure and temperature gradients are used to precipitate the desired material from a high purity feedstock (figure 2(e)). A mineralized solution (e.g., CsF in the case of UO₂) is often used to help transport the nutrient to the substrate where the thin film can crystallize and grow [30, 31]. The main difference between conventional solution growth and hydrothermal synthesis is the viscosity of the liquid. Several actinide compounds have been successfully synthesized using solution approaches, including ThO₂ [32, 33], UN₂ [23], UO₃ [8, 22, 23, 28, 30, 31, 34], U₃O₈ [23], UO₃ [21], UC₂ [23], NpO₂ [23, 24], and PuO₂ [23].

A key challenge associated with solution-based growth approaches is presence of trace amounts of solvent in the final samples. Although the quality of thin films prepared in the last few years is remarkable, further reductions in defect and impurity densities is still a goal for higher precision measurements.

2.3. Physical and chemical vapor deposition methods

Several types of physical vapor deposition (PVD) have been used to synthesize thin films of actinides and surrogate materials (figure 2(c)). Among these, sputtering and electron beam evaporation (EBE) have been most commonly used due to their comparatively low cost and ease of use. Different types of sputtering are used for the deposition of thin films depending on the physical properties of the targets required: radio frequency (RF), DC, high frequency, ion beam, and magnetron sputtering are among the most common. Multiple types can be combined to produce enhanced results in terms of faster deposition rates or more uniform films (figure 2(d)). EBE is commonly used for its ability to heat relatively small areas of a source to very high temperatures, allowing for high precision in deposition rates.

Reactive PVD occurs when a chemical reaction occurs between the deposited material and the atmosphere surrounding the substrate, often during an annealing step. In contrast, pulsed laser deposition (PLD) is a form of PVD where a high power, low bandwidth laser is used to melt, evaporate, and ionize material from the surface of a target [6].

Other techniques used mostly for rare-earth compounds include chemical vapor deposition (CVD) [35, 36] and molecular beam epitaxy (MBE) [37–42]. There have been numerous successful research efforts to use rare-earths as surrogates for actinide materials [43–47]. Similarities in their densities, electronic structure, and high melting temperatures give researchers an opportunity to develop equipment and growth regimes that can be translated from the rare earths to synthesize actinide thin films.

3. Actinide thin films and characterization

Commercial applications of actinide-based compounds depend on a thorough understanding of their properties. This knowledge in turn helps researchers develop ways to synthesize higher quality samples. The accuracy of current physical property measurements for actinide-based materials are limited by defects such as grain boundaries and impurities in the samples. Initial studies of the properties of these materials used polycrystalline samples or, in the best cases, samples with large single crystal grains. Defects such as grain boundaries act as scattering centers for thermal energy carriers (electrons and phonons). Electron- and phonon-mediated conduction processes dictate a material’s thermal and mechanical properties, and understanding these is vital for their full characterization. By eliminating grain boundaries, high quality, single crystalline samples enable researchers to study these processes in the absence of major scattering mechanisms. In addition, the use of new sample geometries and crystallographic orientations continues to expose novel physics and materials properties. For example, controlling dimensionality and strain in actinide heterojunctions will create an opportunity to explore novel quantum phenomena. Here we discuss the promise, challenges, and possible synthesis routes for actinide-bearing heterostructures exhibiting complex electron correlations for functional and energy materials.

3.1. Thin film synthesis

Thin films of actinium metal have been produced since 1953, while thin films of metallic protactinium were synthesized through electrodeposition as early as 1964 [27]. These metallic thin films were used for α-spectrometry and nuclear reaction experiments. Following this work, deposition of thin films of protactinium pentoxide (Pa₂O₅) by electro-spraying was achieved [26].

Reports of thorium-based thin film properties remain relatively scarce due to the absence of a 5f electron orbital. Instead, most attention has focused on thorium’s bulk properties as a candidate fuel for nuclear reactors. With this objective in mind, films of ThO₂ have been synthesized using sputtering [48, 49], photochemical deposition [32], and EBE [50]. Uno et al. used a nitridation approach to synthesize Th₃N₄ [51]. Gouder et al. prepared thin films of ThN and Th₃N₄ using sputter deposition, where photoemission spectroscopy demonstrated a high density of 6d states in ThN and a non-metallic character in Th₃N₄ [52].

UN thin films have been grown via reactive and DC magnetron sputtering using a Nb buffer layer on the (1102) facet of sapphire [53], as well as on Si(111), polycrystalline Ta foil and glass substrates [54]. Black et al. used the same set of substrates [Si(111), polycrystalline Ta foil, and glass] in attempts to grow U₂N₃ [54]. Scott et al. synthesized UN₂ on LAO(001) substrates using PAD [23]. Long et al. also achieved the growth of both of these compounds by nitriding U metal.
flakes [55]. Gouder grew this compound on CaF$_2$ using DC magnetron sputtering [56]. Adamska et al grew UMo films on a Nb(110) buffer layer on a sapphire substrate as well as U–Zr, U–Mo, and U–Nb [57]. The study by Black et al also included thin films of UC$_2$ grown on YSZ(110) and U$_2$O$_8$ in different crystal structures that depended on the orientation of the sapphire substrates [54]. Thin films of uranium oxicarbides and oxinitrides were prepared on Si(111) substrates by Eckle and Gouder using reactive DC sputtering [58]. Two compounds of uranium oxide were grown using PAD on LSAT(100) substrates: $\alpha$-UO$_3$ and $\alpha$-U$_2$O$_9$ [21].

Several attempts at synthesizing UO$_2$ thin films have been reported with various results. The first reported attempt was by Bierlein and Mastel in 1960, where they studied the effects of irradiation by growing UO$_2$ on carbon substrates [59]. Elbakhshwan and Heuser summarized the evolution of UO$_2$ thin film growth up to 2017 [60], and discussed the use of CVD and sputtering techniques (see table 1). Their contribution also includes growth on several different substrates using magnetron sputtering. Further advances in this field since then include reactive sputtering on LSAT(110) [61, 62], magnetron sputtering on YSZ(100) [63], DC sputtering on SrTiO$_3$(110) [64], PAD of UO$_{2+x}$ by Zhang et al [65], and spin coat combustion on aluminum sheets by Roach et al [66]. U$_x$Th$_{1-x}$O$_2$ thin film synthesis was achieved by Cakir et al to study surface reduction using ice [67].

Work on superconducting materials UNi$_2$Al$_3$ and UPd$_2$Al$_3$ realized the first MBE synthesis of actinide containing materials [37–40]. Using electron beam evaporating sources for this materials, depleted U (with no specified purity) was deposited on a heated substrates (listed in table 1) at temperatures of about 700 °C.

Synthesis of transuranic compound thin films has been historically challenging due to the high toxicity and scarcity.
of material precursors [68]. An early attempt to produce thin films of PuO$_2$ is reported by Shaw et al [69]. More recently, Wilkerson et al summarized the state-of-the-art and reported the growth of thin films using PAD on YSZ substrates [70]. Roussel discussed the sputtering of PuO$_2$ and α-Pu$_2$O$_3$ films used to study inverse photoemission [71]. Subsequent attempts to grow bulk single crystals of these oxides used solution based approaches [72–74]. Other Pu-based single crystal compounds synthesized include PuAs, PuSb, and PuBi for studies of anisotropic magnetization [3]. Mannix et al used the same fabrication method to grow NpS and PuSb single crystals to investigate their magnetic structure [75]. Durakiewicz et al investigated the spectral features of USb, NpSb, PuSb, NpTe and PuTe using angle-resolved photoemission spectroscopy (ARPES) on samples grown using a mineralization technique [15]. Gouder et al grew thin films of PuSe and PuSb for study using ultraviolet photoelectron spectroscopy [76], and thin films of PuSi$_x$ (with $x$ varying from 4 to 0.5) [56]. A particularly successful research program involved PAD of PuO$_2$ and NpO$_2$ with high enough crystalline quality that they enabled studies of band dispersion and the Fermi surface, and helped validate several characteristics used in 5f electron modeling approaches [23]. NpO$_2$ was grown on LAO(001) substrates using a UO$_2$ buffer layer. Elements beyond Np have scarcely been fabricated in sufficient amounts to attempt high quality crystal growth. Through a method of oxidation, Radchenko et al managed to fabricate high quality bulk samples of Am, Cm, Bk, and Cf on a La crucible [19].

3.2. Characterization of thin films

We can divide materials characterization techniques into categories that deal with different properties of the thin films in question. Figure 2 illustrates how one can use various techniques to explore structural, surface and electronic properties together in concert.

We can obtain plan view or cross-sectional structural images of a thin film using transmission electron microscopy, scanning electron microscopy (SEM) (see figures 2(c) and (h)), atomic force microscopy, and scanning tunneling microscopy (STM). These can be used to determine the size of crystallites, the density of defects such as dislocations twins and stacking faults, and crystalline quality, in addition to quantifying the roughness of the surfaces and the shape, size and areal density of any structures present on them. ‘Indirect’ structural characterization may include Rutherford back scattering (RBS), XRD, and Raman spectroscopy (see figures 2(a), (d)–(f), (i) and (k)). These techniques can provide information that complements what can be seen in microscopy, and help identify properties such as alloy composition, lattice parameter, and in the case of ion-damaged samples, penetration depth.

Several techniques have been used to measure the thermophysical properties of bulk actinide materials [7]. However, thin films have been targeted in specific cases as a means to increase measurement accuracy while using non-destructive techniques. It is here where photothermal approaches offer a viable option for studying samples with small physical dimensions without damage to the sample or the need for destructive sample preparation approaches [105]. Several comprehensive reviews have been recently published on the thermophysical properties of actinide oxides [7], nitrides [106], and carbides [107, 108] due to the importance of these compounds to nuclear science and industry.

Electronic structure characterization includes angle-resolved photomission spectroscopy (ARPES), x-ray photoemission spectroscopy (XPS), STM-based scanning tunneling spectroscopy (STS), and photoluminescence spectroscopy. These approaches can shed light on charge carrier behavior, and the electronic states present in a given material. These characteristics are of particular interest for actinide thin films due to the interesting physics governed by their 5f electron states. XPS allows one to determine the elements present within a material, along with their oxidation and bonding state. XPS is especially useful for samples with reduced dimensionality within which the localization of 5f electrons occurs [109]. Gouder and Havela identified the complications of applying XPS to the study of actinides: an asymmetrical tail in metallic systems can often prove difficult to differentiate from scattering of electrons onto the Fermi level. In addition, the anisotropic distribution of atoms at different temperatures contributes to higher noise levels in the XPS signal [109]. The team lead by Black et al identified the 5f states of UN around 0.8 eV [54]. Havela et al indicate that 5f localization behavior can be studied in PuSb (localized), PuSe (intermediately localized), and PuN (potentially delocalized) [96]. In addition, Gouder et al studied the localization of 5f electrons in PuSi, [89]. Durakiewicz et al investigated the systematic changes in the 5f binding energy peak between antimonide and tellurides of U, Pu, and Np [15]. Joyce et al studied the dual nature of 5f electrons using photoemission of δ-Pu, PuI$_3$, and PuCoGa$_5$ [110, 111]. On the same line, Eliordi et al reported results from XPS studies of PuCoGa$_5$ deposited using sputtering [112]. Long et al studied the electronic structure of α-U$_2$N$_3$ and found hints of metallic bonding [81]. Pentavalent uranium was found in U$_2$O$_3$ by Gouder et al using photoemission studies [113].

The ARPES technique has been used to determine precise band structures and Fermi surfaces of actinide-based single crystals [23, 98, 114–137]. Largely focused on bulk actinide compounds, these ARPES studies have created new opportunities for determining the origin of the unusual physical properties of 5f-electron materials. Going forward, ARPES-based studies of epitaxial actinide thin films could lead to the discovery of a wide range of emerging electronic, magnetic, and structural phenomena (figure 2(j)). Interactions between the epitaxial thin film and the underlying substrate can produce properties that are substantially different from those of the bulk materials. For instance, it has been reported that one can obtain an unusual hexagonal close-packed phase of uranium (hcp-U) by depositing U thin films onto a W (110) substrate [138, 139]. Theoretical calculations predict that the hcp-U phase has an electronic instability, that could lead to a possible
charge density wave or magnetic ordering [140]. Different orientations of the α-U orthorhombic phase can also be obtained by depositing U onto a variety of buffer/seed layers on sapphire substrates [92, 141]. ARPES was used to obtain the band structure of α-U single crystals at 173 K [142]. The valence band structure of α-U was studied in details using ultraviolet photoemission spectroscopy and XPS [143]. For ordered overlayers of U metal grown on a W (110) substrate, band-like properties of the U 5f states were observed, which were proposed to arise from direct f–f electron interactions [138]. STM/STS results showed that the U density of states close to the Fermi level is dominated by the 5f states [139]. STS and ARPES showed both the Fermi surface topology and electronic structure of ordered α-U films [144]. ARPES studies of epitaxial thin films of the oxides PuO₂ and NpO₂ [24, 145], and uranium carbide (UC₂), reveal the importance of the underlying substrate structure in stabilizing the epitaxial film [146]. But in general, compared with bulk actinide crystals, only a few ARPES studies have been performed on actinide thin films. Therefore, the use of ARPES to measure novel actinide thin films synthesized with higher quality will produce results that are critical to understanding their reactivity, aging, nuclear fuel behavior, and environmental fate, as well as the potentially rich physics of these exotic 5f materials.

4. Thermophysical, magnetic, and topological properties of actinide thin films

4.1. Thermophysical properties

Thermophysical properties play a central role in determining the characteristics of actinide materials. Atomic structure dictates macroscopic behavior, and it is hence important to understand the temperature dependence of these properties. A key research driver in actinide compounds is the qualification process for nuclear fuel materials. This process is heavily reliant on characterizing thermophysical properties: heat capacity, thermal conductivity, elastic constants, and thermal expansion [7, 147]. Heat capacity has been measured in several important actinide dioxides, such as ThO₂ [105], UO₂ [148], NpO₂ [149], PuO₂ [150]. UO₂ and NpO₂ show interesting magnetic alignment transition that creates anomalies in their heat capacity. Thermal conductivities have been measured for ThO₂ [151], UO₂ [152], NpO₂ [153], and PuO₂ [154]. The heat capacities of select actinide nitride systems have been measured, including ThN [155], and more recently for the UN–ThN mixtures used in nuclear fuels [106]. Among these properties, thermal diffusivity and conductivity have been recently studied as important factors in determining the properties of a nuclear fuel candidate material [7]. The qualification process requires that intrinsic thermophysical properties be resolved independently of any particular specimen geometry, without the competing influence of lattice defects or other chemical or structural imperfections. Building a fundamental understanding of intrinsic properties allows for the effects of these additional complexities, for example the types of structural defects generated under exposure to irradiation, to be systematically included in computational frameworks for engineering-scale performance. Much success to date has been found in the use of non-destructive photothermal techniques to measure these intrinsic thermophysical properties [105]. Such methods broadly consider microscale thermal and acoustic wave propagation, which can be measured via surface deformation, refractive index gradient, acoustic expansion/contraction, or changes in optical reflectivity (thermoreflectance). This last approach can be further subdivided into frequency-domain thermoreflectance, time-domain thermoreflectance, spatial-domain thermoreflectance, and hybrid methods [147, 156]. With small sampling volumes, these methods are broadly applicable to the study of thin films [157]. Although they have not yet been applied to actinide thin films, we anticipate that these techniques will help to shed light on their thermophysical properties in the future.

Heterostructure devices that integrate different functional layers can encounter performance issues as a result of restricted heat dissipation across the heterointerfaces (Kapitza resistance). This restriction in heat dissipation correlates with factors such as interfacial roughness, disorder, dislocations, and bonding. As a result, computational modeling of these interfaces often fails to capture all of their vibrational properties, for example changes in mass density, phonon mean free path, and carrier scattering across the interface [158] (figure 3).

4.2. Magnetic properties

Different aspects of electron and phonon behavior have been carefully studied under the influence of magnetic fields. Among these, transport and its different manifestations enabled the observations of several noteworthy phenomena. These physical properties are part of what makes actinides interesting to researchers beyond their nuclear applications [159]. Most transition metal elements have itinerant d electrons, while lanthanide elements exhibit mostly localized 4f electrons. These facts help us distinguish characteristics related to the conduction band of a material, and its magnetic properties relating to the 4f electrons [159]. Due to the scarcity, high cost of 232Th and intense radioactivity single crystal samples of this metal have not been synthesized to date, making it difficult to study its magnetic properties experimentally [160]. A similar situation exists for the actinide elements after californium.

Considering the intervening elements, Th is a paramagnetic metal with three phases that are heavily influenced by the concentration of impurities present [1]. Pa metal was synthesized relatively early on in the development of actinide research, and it was hence possible to determine its phase transition and superconducting behavior [1], as discussed below. The early actinide metals (U, Np, Pu) show no sign of magnetic ordering mostly because the bandwidth of the 5f electrons in these elements is too wide to satisfy the Stoner criterion [161]. U metal exhibits a weak Pauli-type paramagnetism, with α-U having a charge-density-wave anomaly around 43 K that has been observed in magnetic susceptibility measurements [1]. Np exhibits spin–orbit coupling in the same order as other
crystal-related electric effects, leading to its metallic form and paramagnetic behavior [1]. Elemental Pu can be found in both α- and δ-Pu phases. Recent studies point to a lack of evidence favoring any ordered or disordered magnetism in δ-Pu [162], which preferentially forms a valence fluctuation ground state [163]. Am metal shows a non-magnetic ground state coming from the 5f⁶ electronic configuration (J = 0). Curium (Cm) is the first element in the actinide series that orders magnetically. Cm is antiferromagnetic (AF) below 65 K in the double hexagonal close packed (dhcp) phase, while in the fcc phase it is ferromagnetic (FM) below 205 K [164]. Berkelium (Bk) also exists in these two crystallographic phases (dhcp and fcc) and similarly orders either AF or FM. Californium (Cf) also exhibits a large effective magnetic moment, similar to Cm and Bk, and likely has a FM ground state [165].

A variety of thin films of actinide compounds have provided insight into the magnetic properties of these systems, such as the magnetic structures of NpS and PuSb [75], itinerant antiferromagnetism [77] and magneto-optical Kerr effect [166] in UN, weak ferromagnetism [167] and antiferromagnetism [82] of UO₂, and the high pressure behavior of electrical resistance in NpAs and NpBi [168]. Single crystal compounds have shown to have different critical temperatures for magnetic reordering [37], and special epitaxial compounds such as UNi₂Al₃ have demonstrated superconductivity at 0.97 K [40]. Magnetic susceptibility measurements of transplutonium elements Am, Cm, and Bk helped determine the effective magnetic moments and Curie–Weiss constants for some of their compounds [169]. Magnetic properties have also been extensively studied in these materials using computational methods ([170] and references therein). Bright et al studied the magnetic and electronic structure of UN and U₂N₃ epitaxial films using x-ray scattering [171]. Recently, using high-field magnetization and magnetostriction measurements, the presence of a metamagnetic transition and a tri-critical point was observed in UN single crystals, leading to the development of a magnetic phase diagram for this material [172, 173]. Using micro-structured single crystals, Hamann et al found strong reconstruction of the Fermi surface at the high-field transition [174].

4.3. Superconductivity

Certain actinide metals are known to exhibit superconductivity at low temperature. These include Th at 1.4 K [175],

Figure 3. Properties of interest in select actinide thin films considered in this review. Under thermophysical properties, measurements of heat capacity in some actinide oxides exhibit an anomaly at certain phase transition temperatures. Magnetic properties to consider include the quantum, quantum anomalous, and quantum spin Hall effects. Two important topological properties are superconductivity (present in the UP₃ compound, and topologically protected states) together with topological insulators in two and three dimensions, respectively. Reprinted with permission from [7]. Copyright (2022) American Chemical Society.
Pu at 1.4 K [176, 177], α-U at 0.7 K and γ-U at 1.8 K [2, 178–180]. Am was predicted to be a superconductor, although confirming this experimentally was a challenge due to its large self-heating, scarcity, and radioactivity. However, this prediction was confirmed by Smith and Haire; when its fcc phase is stabilized by impurities, Am becomes superconducting at 1.05 K, and pure dhcp Am is superconducting at 0.79 K [181]. α-Np and α-Pu have no reported superconducting signature down to 0.5 K [182] and Cm, Bk, and Cf are not expected to show superconductivity because of their magnetic ground state [182]. There are several actinide compounds that show heavy-fermion superconductivity, including UBe13, UPt3, URu2Si2, UNi2Al3, UPd2Al3, NpPd5Al2, PuCoIn4, PuRhGa5, PuRhIn5 and PuCoGa5 [98, 183–190]. Ott et al. showed that UBe13 is superconducting below 0.85 K [191]. Joyce et al. studied photoemission data from PuCoGa5, PuIn3, and δ-Pu metal. A comparison between their results and model studies indicate characteristics of both itinerant and localized Pu 5f electrons [110]. Furthermore, Joyce compared Tc in PuCoGa5 against UCoGa5 and found no evident characteristics of strongly correlated electrons [111]. Thus, valence fluctuations have been proposed as an alternative mechanism for the high-temperature superconductivity observed in PuCoGa5 [192, 193]. Recently, unconventional [194], spin-triplet [195] superconductivity with multiple superconducting phases [196] has been reported in UTe2. In addition, there are indications for spontaneously broken time-reversal symmetry [197], and chiral Majorana edge and surface states [198], the nature of which are not yet understood. Bruno, Cren, and Roditchev summarized the superconductivity of 2D materials as a strong case for epitaxial monolayer materials growth [199]. Huth et al. demonstrated deviations from typical heavy-fermion material characteristics in superconducting UPt3 [91], attributed to the hybridization of 5f electrons and itinerant states, although the nature of the pairing mechanism is still under debate. Superconductivity was also observed in UPd2Al3 [38] and UNi2Al3 [40], while the optical conductivity of this last compound was studied by Ostertag et al using terahertz frequencies [200].

4.4. Topological properties

The study of conducting states in topologically nontrivial materials is often hindered by the presence of bulk conducting states [201]. High quality thin films offer one way of minimizing bulk contributions by increasing a sample’s surface area-to-volume ratio, simplifying measurements of these topological effects. Due the nature of their electronic structure, actinide materials represent a fascinating, albeit challenging area for topological discoveries. Promising technological applications and insights into fundamental physics continue to motivate investigations on the complex manifold of 5f, 6p, 6d, and 7s orbital shells [202]. These interactions, present in an analogous manner in the rare earths, are expected to give rise to a variety of topological behaviors in different compounds and geometries.

Heavy fermion materials owe their particular properties to the competition between Coulomb repulsion of localized f electrons, and hybridization with itinerant d electrons. These electron correlations produce complex states including Mott physics, superconductivity, and correlated magnetism [203]. Understanding these electronic systems could potentially help elucidate other strongly correlated electron materials, for example high-temperature superconductors, multiferroics, and magnetoresistive materials. Topological insulators possess conducting surface states protected by the non-trivial topological property of spin-momentum locking. Several quantum materials have been proposed based on topological properties that involve quantum phenomena such as Majorana fermions, the anomalous quantum Hall effect, with applications in spintronics and fault tolerant quantum computation. Magnetic topological semimetals have been synthesized using MBE [204, 205]. These materials have a FM ground state that breaks time-reversal symmetry with a gap in the topological surface states [206]. A powerful tool to study these phenomena is density functional theory (DFT), e.g. its use in identifying phases in UNiSn corresponding to a topological insulator and a Weyl semimetal depending on magnetic ordering [207]. Rocksalt compounds of Pu and Am were predicted to form a topologically insulating ground state due to their 5f electron being right on the boundary between localized and itinerant, and coupling between electronic and spin–orbit interactions gives rise to band gap formation [208]. The predicted compounds that Zhang et al. used for this study include americium monopnicdites and plutonium monochalcogenides [208]. Using nuclear magnetic resonance, Dioguardi et al. demonstrated that PuB4 is a strong candidate for a topological insulator, which has also been suggested by Choi et al. [209, 210]. Recent theoretical work suggests that the intermediate valence PuB6 is a strong topological insulator with nontrivial Z2 topological invariants [211], similar to SmB6 [212].

Overall, much work is still to be done in understanding fully the properties of these actinide compounds, and high quality thin films promise to be the missing piece to provide a window into their discovery.

5. Challenges with modeling 5f electrons

DFT [213, 214] is normally the zeroth level of first-principles theory that is applied to any material, given the relatively small computational cost for the degree of complexity it can capture [215, 216]. DFT has found success across the periodic table for calculating a myriad of materials properties [217–220]. Unfortunately, all known implementations of DFT have well-known limitations [221–223]. In particular, DFT sometimes qualitatively breaks down for certain properties in materials bearing strongly correlated electrons. For example, Mott insulators are often incorrectly predicted to be metals by DFT [224]. Materials with f-electrons are ripe for strongly correlated electron physics, due to the relatively narrow bands.
formed by the f-orbitals and large on-site Coulomb repulsion. Other limitations for DFT calculations, particularly in strongly correlated systems, include the inability to properly capture finite temperatures and excited states [225].

Fortunately, dynamical mean-field theory (DMFT) [226] can overcome many of the shortcomings of DFT. DMFT can also be applied to real materials when combined with DFT to yield the DFT + DMFT formalism [222]. DMFT requires the solution of a quantum impurity problem, which is associated with the correlated shell of electrons (e.g., f-electrons). These solutions can be achieved in realistic multiorbital problems using continuous time quantum Monte-Carlo (CTQMC) [227–229]. While DFT + DMFT (CTQMC) is far more computationally expensive than DFT, current algorithms and computing power allow for calculations in relatively complex systems bearing d and f electrons [230–235]. An efficient, but far less accurate solution of the DMFT impurity problem can be achieved with the Hartree–Fock method. This method yields the better known DFT + U approach [222, 236], for which the computational overhead is negligible when compared to DFT. Together, DFT, DFT + DMFT, and DFT + U form a hierarchy of first-principles approaches that serve as the basis for parameterizing multiscale models to generate information at longer length and time scales [237] (figure 4).

Compared with bulk materials, the surfaces and heterostructures associated with thin films introduce additional complexity to modeling efforts due to confinement effects, charge transfer, strain, and structural reconstruction. When considering actinide thin films, the presence of f-electrons in these systems contributes yet another layer of complexity. In actinide oxides, a wide range of phenomena have been observed in thin film heterostructures that are absent from their bulk constituents. These phenomena include superconductivity [240, 241], room temperature ferromagnetism [242], metal–insulator transitions [243], and orbital reconstruction [244], with the clear potential for novel device physics [245]. DFT + U and DFT + DMFT have already been used to confirm emergent properties in heterostructures composed from transition metal oxides [246–248]. However, similar calculations for heterostructures built from f-electron materials will undoubtedly be more challenging than those for d-electron materials. The DFT + DMFT computations will be substantially more computationally expensive, and DFT + U computations will struggle with a more treacherous energy landscape. Nonetheless, f-electron heterostructures are within reach of our present theories and computational resources, and there has already been some progress at the level of DFT. Gao and Ray used DFT to study the (001) [249], and (111) [250] surfaces of Am. The surface properties of UN, a candidate nuclear fuel, have been studied using DFT + U, with potential applications for understanding corrosion characteristics [251]. In short, a combination of models based on DFT, DFT + U, and DFT + DMFT are well poised to study heterostructures composed from f-electron material thin films, and will lay the foundation for understanding such materials.

Optimization of algorithms based on strongly correlated electron systems in DFT will provide more accurate descriptions of physical systems, able to in turn provide higher level modeling systems a path toward integration with engineering-level modeling paradigms based on first principles.

6. Future directions: thin film heterostructure synthesis and challenges

Interfaces in semiconducting, metallic, and semi-metallic materials offer possibilities for investigating electronic properties not typically present in the bulk, or in layers of a single material. In non-actinide semiconductors, heterostructures built by stacking different thin films have enabled researchers to discover new physics. For example, thin films and other low dimensional heterostructures allow to study the quantum behavior of charge carriers whose de Broglie wavelength is equivalent to the size of the potential well within which they are confined. A deeper understanding of how we can manipulate charge carrier behavior using heterostructures led to the design of entirely new electronic and photonic devices. Indeed, Kroemer famously stated that in these heterostructures, the interface is the device [252]. Extending heterostructure growth to actinide-based compounds therefore promises to enable researchers to study these materials in new ways. For example, low-dimensional heterostructures composed of actinide materials with 5f electrons, grown with interfaces containing tailored defect densities, represent a fertile area for the discovery of various emerging phenomena [253]. Studies have predicted a range of exotic physics for such structures, including highly correlated electron interactions [202, 254], topological insulator behavior [207, 210], and confined 2D properties [255, 256].

As we have seen, the synthesis of high quality, atomically precise thin films of a single actinide material is still the focus of ongoing research. As a consequence, the ability to routinely and controllably integrate two or more of these thin films to create actinide heterostructures remains largely an area for future development. Before one can begin to study the characteristics of these heterostructures, one must first be able to produce high purity films with uncontaminated interfaces. Controlling interactions at the interface between two films requires a consideration of atomic intermixing, surface energies, charge transfer, and epitaxial nucleation and growth. These effects will likely be a function of the environment within which a heterostructure is synthesized [257]. Solution- and chemical reaction-based synthesis approaches, for example, often leave residues of unwanted atomic species during deposition. For this reason, physical deposition methods offer perhaps the best route to achieving pristine thin film formation, and hence heterostructure synthesis. Due to its rapid output and relatively low cost, PLD offers a convenient test-bed for initial film and substrate screening studies. After some of the film–substrate combinations predicted by theory have been demonstrated experimentally, even higher quality films can be grown using MBE, which uses ultrahigh purity elemental source materials rather than chemical precursors or solutions. The advantages of MBE include exceptionally
high material purity, and exquisite control over layer thickness and interfacial abruptness, both of which are prerequisites for growing functional heterostructures. To our knowledge, the only reports for actinide MBE are those of Huth et al. [37], Jourdan et al. [39], and Zakharov et al. [40].

The epitaxial challenges for integrating different materials include lattice constant mismatch, dissimilar crystal structures, thermal expansion differences, and incompatible growth environments. Several strategies have been devised to overcome strain-related issues arising from lattice mismatch. These include the use of graded buffers [258, 259], interfacial misfit arrays [260], self-assembled quantum dots [261], alloying [262], lattice constant mismatch inversion [263], and strain-relieving superlattices [264]. To accommodate different crystal structures, a common crystal lattice parameter can be used to geometrically align the lattices between each layer. An example is the differing crystal structures of ErAs (rocksalt) and InGaAs (zincblende). A rotation of the ErAs unit cell with respect to that of the InGaAs brings the two lattices into registry, enabling the growth of coherent ErAs/InGaAs heterostructures [265]. Mismatch between thermal expansion coefficients in different layers of the heterostructure can induce strain upon sample cooling, which is then relaxed through defect formation, negatively impacting crystal quality. Common solutions to this challenge include growth of thin protective thermal layers that prevent these relaxation processes, and use of thermally pre-stressed films that can accommodate the strain upon the change in temperature [266]. It will be critical to consider all of these challenges and solutions as researchers begin to explore the synthesis of actinide-based thin film heterostructures.

To fill this technological gap, the Idaho National Lab has recently commissioned an MBE system designed specifically for the growth of actinide–nitride compounds. This first-of-its-kind MBE system will permit feasibility studies of the growth of various actinide-based thin films. Proof-of-concept experiments will target the MBE growth of heterostructures based on UN and ThN (figure 5). These heterostructures will
enable the study of the electronic properties of these interesting 5f-electron heterointerfaces. Given the lattice mismatch of \( \sim 5.7\% \) between UN and ThN, the substrate material must be chosen carefully to allow growth of layers with reasonable thickness, while remaining below the Matthews–Blakeslee limit for strain relaxation [267].

An alternative approach is to create heterostructures based on U\(_7\)-Th\(_{1-x}\)-N alloys that have lower lattice mismatch to the binary end-point compounds. To this end, table 2 lists a ‘recipe book’ of actinide nitrides and candidate substrates with reasonably lattice-matched alloys. Indeed, by incorporating suitable buffer layers, some of these compound/substrate combinations have already been synthesized [53]. The hope is that by exploring the MBE growth of materials in these actinide nitride systems, their thermophysical, magnetic, and topological properties can be studied with high precision. Actinide–nitride-based systems that show promising initial results will be screened for emergent phenomena, with a view to opening a new approach to investigating the interplay between electronic correlations and topology in epitaxial thin films and heterostructures.

7. Outlook

Recent years have seen significant advances in the field of actinide materials synthesis. Ongoing improvements in materials growth techniques are beginning to produce single-crystal samples of actinide metals and their compounds. These efforts include the synthesis of both bulk crystals and thin films, within which grain boundaries are eliminated and the density of other crystallographic defects is reduced. Syntheses using a variety of methods have been demonstrated important initial material compatibility criteria (temperature ranges, lattice constants, etc) for reliable thin film synthesis. As a result, researchers can, for the first time, investigate thermal and electrical transport properties of actinides in samples with dramatically reduced phonon and electron scattering. In the near term, concerted efforts are being made to integrate different thin film actinides into heterostructures whose properties can be tuned through strain, confinement and other interfacial effects. The expectation is that, as a result, the subtle physical features of these materials will begin to emerge. Exotic magnetic and topological properties are expected to arise in these strongly correlated systems with 5f-shell electrons, leading to the discovery of new physics.

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### Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Morss L R, Edelstein N M, Fuger J and Katz J J 2006 The Chemistry of the Actinide and Transactinide Elements vol 1 (Springer)

[2] Moore K T and van der Laan 2009 Nature of the 5f states in actinide metals Rev. Mod. Phys. 81 235

[3] Mattenberger K, Vogt O, Spiret J C and Rebizant J 1986 Anisotropic magnetization of PuAs, PuSb and PuBi single crystals J. Magn. Magn. Mater. 54–57 539–40

[4] Stewart G R 1984 Heavy-fermion systems Rev. Mod. Phys. 56 755

[5] Stewart G R 2001 Non-Fermi-liquid behavior in d- and f-electron metals Rev. Mod. Phys. 73 797

[6] Enriquez E et al 2020 Structural and optical properties of phase-pure UO₂, α-U₂O₆, and α-UO₃ epitaxial thin films grown by pulsed laser deposition ACS Appl. Mater. Interfaces 12 35232–41

[7] Hurley D H et al 2022 Thermal energy transport in oxide nuclear fuel Chem. Rev. 122 3711–62

[8] Rickert K, Velez M A, Prusnick T A, Turner D B, Kimani M M, Bowen T and Mann J M 2021 Hydrothermal crystal growth on non-native substrates: the case of UO₂ Cryst. Growth Des. 21 6289–300

[9] Gouder T 1998 Thin layers in actinide research J. Alloys Compd. 271–273 841–5

[10] Modyanselage K, Burrell A K, Senanayake S D and Idriss H 2019 XPS and NEXAFS study of the reactions of acetic acid and acetaldehyde over UO₂(100) thin film Surf. Sci. 680 107–12

[11] Spiret J C and Vogt O 1982 Preparation of actinides and actinide compounds J. Magn. Magn. Mater. 29 31–8

[12] Clark D L, Geeson D A and Hanrahan R J 2019 Plutonium Handbook vol 6 (Illinois: American Nuclear Society)

[13] Edwards C R and Oliver A J 2000 Uranium processing: a review of current methods and technology J. Miner. Met. Mater. Soc. 52 12–20

[14] Glover K M and Burrell P 1955 A method for the preparation of thin films of plutonium and uranium J. Nucl. Energy 1 214–7

[15] Durakiewicz T et al 2004 Electronic structure of actinide antimonides and tellurides from photoelectron spectroscopy Phys. Rev. B 70 205103

[16] Farr J D, Giorgi A L, Bowman M C and Money R K 1953 The crystal structure of actinum metal and actinium hydride Technical Report (Los Alamos, NM: Los Alamos National Laboratory (LANL))

[17] Bowman A L and Arnold G P 1971 The crystal structure of ThN₄ Acta Crystallogr. B 27 243–4

[18] Tagawa H and Masaki N 1974 X-ray and density studies of nonstoichiometric uranium sesquisnitrinitride J. Inorg. Nucl. Chem. 36 1099–103

[19] Radchenko V M, Ryabinin M A and Stupin V A 2010 Production and investigation of thin films of metal actinides (Pu, Am, Cm, Bk, Cf) IOP Conf. Ser.: Mater. Sci. Eng. 9 012034

[20] Danilin I D, Kartushin V D, Pilipenkov N V, Abramycheva I D and Vensovskii S P 2002 Production of films of uranium and americium compounds by thermal decomposition of volatile β-diketonates Nucl. Instrum. Methods Phys. Res. A 480 75–8

[21] Kruk I, Scott B L, Watkins E B and Wolsfberg L E 2021 Growth and characterization of uranium oxide thin films deposited by polymer assisted deposition Thin Solid Films 735 138874

[22] Burrell A K, McCleskey T M, Shukla P, Wang H, Durakiewicz T, Moore D P, Olson C G, Joyce J J and Jia Q 2007 Controlling oxidation states in uranium oxides through epitaxial stabilization Adv. Mater. 19 3559–63

[23] Scott B L, Joyce J J, Durakiewicz T D, Martin R L, McCleskey T M, Bauer E, Luo H and Jia Q 2014 High quality epitaxial thin films of actinide oxides, carbides, and nitrides: advancing understanding of electronic structure of f-element materials Coord. Chem. Rev. 266–267 137–54

[24] McCleskey M T et al 2013 Optical band gap of NpO₂ and PuO₂ from optical absorbance of epitaxial films J. Appl. Phys. 113 013515

[25] Getoff N and Bildstein H 1966 The preparation of thin films of tantalum and protactinium by electro spraying Inorg. Nucl. Chem. Lett. 2 1–3

[26] Shimoinuma H and Takagi J 1964 Electrodeposition of protactinium J. Inorg. Nucl. Chem. 26 253–5

[27] Qiu S R, Amrhein C, Hunt M L, Pfeffer R, Yakshinskii B, Zhang L, Madey T E and Yarmoff J A 2001 Characterization of uranium oxide thin films grown from solution onto Fe surfaces Surf. Appl. Surf. Sci. 181 211–24

[28] Laudise R A 2004 Hydrothermal synthesis of crystals 50 Years Progress in Crystal Growth (Amsterdam: Elsevier) p 268

[29] Young C, Petrosky J, Mann J M, Hunt E M, Turner D and Kelly T 2016 The work function of hydrothermally synthesized UO₂ and the implications for semiconductor device fabrication Phys. Status Solidi 10 687–90

[30] Dugan C L et al 2018 Electrical and material properties of hydrothermally grown single crystal (111) UO₂ Eur. Phys. J. B 91 67

[31] Huentupil Y, Cabello-Guzmán G, Chornik B, Arancibia R and Buono-Core G E 2019 Photochemical deposition, characterization and optical properties of thin films of ThO₂ Polyhedron 157 225–31

[32] Rickert K, Prusnick T A, Hunt E, French A, Turner D B, Bennett C A, Shao L and Mann J M 2022 Raman and photoluminescence evaluation of ion-induced damage uniformity in ThO₂ Nucl. Instrum. Methods Phys. Res. B 815 69–79

[33] Majumdar A, Manukyan K V, Dede S, Roach J M, Robertson D, Burns P C and Aprahamian A 2021 Irradiation-driven restructuring of UO₂ thin films: amorphization and crystallization ACS Appl. Mater. Interfaces 13 35153–64

[34] Straub M D, Leduc J, Frank M, Raufaß A, Lohrey T D, Minasian S G, Mathur S and Arnold J 2019 Chemical vapor deposition of phase-pure uranium dioxide thin films from uranium(IV) amide precursors Angew. Chem., Int. Ed. 58 5749–53

[35] Raufaß A, Leduc J, Frank M, Stadler D, Graf D, Wilhelm M, Grosch M and Mathur S 2021 Magnetic field-assisted chemical vapor deposition of UO₂ thin films Inorg. Chem. 60 1915–21

[36] Huth M, Kaldowski A, Hessert J, Steinborn T and Adrian H 1993 Preparation and characterization of thin films of the heavy fermion superconductor UPd₄Al₃ Solid State Commun. 87 1133–6

[37] Huth M, Kaldowski A, Hessert J, Heske C and Adrian H 1994 UPd₄Al₃ heavy fermion superconducting films Physica B 199 116–8

[38] Jourdan M, Zakharov A, Foerster M and Adrian H 2004 Preparation of thin films of the heavy fermion superconductor UNi₁Al₃ J. Magn. Magn. Mater. 272–276 E163–4

[39] Zakharov A, Jourdan M, Foerster M and Adrian H 2005 Preparation of superconducting thin films of UNiAl Physica B 359–361 1108–10

[40] Ragnarsson L-Å, Guha S, Copel M, Cartier E, Bojarzuk N A and Karasinski J 2001 Molecular-beam-deposited yttrium-oxide dielectrics in aluminium-gated metal-oxide-semiconductor field-effect transistors: effective electron mobility Appl. Phys. Lett. 78 4169–71

[41] Tarnawska L, Giussani A, Zaussel P, Schubert M A, Paszkiewicz R, Brandt O, Storck P and Schroeder T 2010
[128] Chatterjee S, Trinckauf J, Hänke T, Shai D E, Harter J W, Williams T J, Luke G M, Shen K M and Heck J 2013 Formation of the coherent heavy fermion liquid at the hidden order transition in $\text{URu}_2\text{Si}_2$ Phys. Rev. Lett. 110 186401

[129] R Yoshida K T, Ishiga T, Sunagawa M, Sonoyama J, Aoki D, Floquet Q, Wataki T, Muraoka Y and Yokoya T 2013 Translational symmetry breaking and gapping of heavy- quasiparticle pocket in $\text{URu}_2\text{Si}_2$ Sci. Rep. 3 2750

[130] Meng J-Q, Oppeneer P M, Mydosh J A, Riseborough P S, Gořyk K, Joyce J J, Bauer E D, Li Y and Durakiewicz T 2013 Imaging the three-dimensional Fermi-surface pairing near the hidden-order transition in $\text{URu}_2\text{Si}_2$ using angle- resolved photoemission spectroscopy Phys. Rev. Lett. 111 127002

[131] Bareille C, Boariu F L, Schwab H, Lejay P, Reinert F and Santander-Syro A F 2014 Momentum-resolved hidden- order gap reveals symmetry breaking and origin of entropy loss in $\text{URu}_2\text{Si}_2$ Nat. Commun. 5 4326

[132] Durakiewicz T 2014 Photoemission investigations of $\text{URu}_2\text{Si}_2$ Phil. Mag. 94 3723–36

[133] Ruello P, Becker K D, Ulrich R, Desgranges L, Petot C and Petot-Eras G 2004 Thermal variation of the optical absorption of $\text{URu}_2\text{Si}_2$ determination of the small polaron self-energy J. Nucl. Mater. 328 46–54

[134] Tobin J G and Yu S-W 2011 Orbital specificity in the unoccupied states of $\text{UO}_2$ from density functional theory calculations: structural, magnetic and electronic properties of $\text{U}(001)$ thin films Surf. Interface Anal. 43 26–32

[135] Joyce J J, Arko A J, Cox L E and Czuchlewski S 1998 Resonance photoelectron spectroscopy of single-crystalline uranium thin films on W(110) Surf. Interface Anal. 26 121–3

[136] Molodtsov S L, Boysen J, Richter M, Segovia P, Laubschat C, Yoshida K T, Ishiga T, Sunagawa M, Sonoyama J, Aoki D, Floquet Q, Wataki T, Muraoka Y and Yokoya T 2013 Absence of magnetic moments in plutonium Comp. Mag. 209 1–6

[137] Janoschek M, Lashley J C, Lawson A, McQueeney R J and Lander G H 2005 Determining local thermal transport in a composite uranium-nitride/silicide nuclear fuel using square-pulse transient thermoreflectance technique J. Nucl. Mater. 334 151842

[138] Sanati M, Albers R C, Lookman T and Saxena A 2011 Elastice constants, phonon density of states, and thermal properties of $\text{UO}_2$ Phys. Rev. B 84 014116

[139] Santini P, Carretta S, Amoretti G, Caciuffo R, Magnani N and Lander G H 2009 Multipolar interactions in f-electron systems: the paradigm of actinide dioxides Rev. Mod. Phys. 81 807

[140] Magnani N, Santini P, Amoretti G and Caciuffo R 2005 Perturbative approach to j mixing in f-electron systems: application to actinide dioxides Phys. Rev. B 71 054105

[141] Mann M, Thompson D, Serivalisat K, Tritt T M, Ballato J and Kolis J 2010 Hydrothermal growth and thermal property characterization of $\text{ThO}_2$: single crystals Cryst. Growth Des. 10 2146–51

[142] Göfryk K et al. 2014 Anisotropic thermal conductivity in uranium dioxide Nat. Commun. 5 4551

[143] Nishi T, Itoh A, Numata M, Akabori M, Arai Y and Minato K 2008 Thermal conductivity of neptunium dioxide J. Nucl. Mater. 376 78–82

[144] Lagedrost J F, Askey D F, Storhok V W and Gates J E 1968 Thermal conductivity of $\text{PuO}_2$ as determined from thermal diffusivity measurements Nucl. Appl. 4 54–61

[145] Parker S S, White J T, Hosenmann P and Nelson A T 2019 Thermophysical properties of thorium monocarbide from 298 to 1700 K J. Nucl. Mater. 526 151760

[146] Khafizov M, Chauhan V, Wang Y, Riyad F, Hang N and Hurley D H 2017 Investigation of thermal transport in composites and ion beam irradiated materials for nuclear energy applications J. Mater. Res. 32 204–16

[147] Luckyanova M N, Johnson J A, Maznev A A, Garg J, Jandi A, Bulsara M T, Fitzgerald E A, Nelson K A and Chen G 2013 Anisotropy of the thermal conductivity in Ga2Al3As2 superlattices Nano Lett. 13 3973–7

[148] Giri A, Braun J L and Hopkins P E 2016 Effect of crystalline/amorphous interfaces on thermal transport across confined thin films and superlattices J. Appl. Phys. 119 235305

[149] Santini P, Lemanski R and Erkös P 1999 Magnetism of actinide compounds Adv. Phys. 48 537–653

[150] Debloonde G J P, Zavarin M and Kersting A B 2021 The coordination properties and ionic radius of actinium: a 120 year-old enigma Coord. Chem. Rev. 446 214130

[151] Severin L, Brooks M S S and Johansson B 1993 Relationship between the Coulomb integral $U$ and the Stoner parameter I Phys. Rev. Lett. 71 3214

[152] Lashley J C, Lawson A, McQueeney R J and Lander G H 2005 Absence of magnetic moments in plutonium Phys. Rev. B 72 054416

[153] Janoschek M et al 2015 The valence-fluctuating ground state of plutonium Sci. Adv. 1 e1500188

[154] Lander G H et al 2019 Measurements related to the magnetism of curium metal Phys. Rev. B 99 224419

[155] Ott H R, Fisk Z, Freeman A J and Lander G H 1987 Handbook on the Physics and Chemistry of the Actinides (Amsterdam: North-Holland) pp 85–225

[156] Marutzky M, Barkow U, Schoenes J and Troc R 2006 Optical and magneto-optical properties of single crystalline uranium nitride J. Magn. Magn. Mater. 299 225–30
[167] Sakai H, Kato H, Tokuanga Y, Kambe S, Walstedt R E, Nakamura A, Tateiwa N and Kobayashi T C 2004 Magnetism of uranium dioxide UO2 under high pressure J. Magn. Magn. Mater. 272 E413–4

[168] Ichas V, Zvirner S, Braithwaite D, Spirelt J C, Rebizant J and Potzel W 1997 Electrical resistance and magnetic properties of the neptunium mononitrides NpAs, NpSb, and NpBi at high pressures Phys. Rev. B 56 14481

[169] Nave S E, Haire R G and Huray P G 1983 Magnetic properties of actinide elements having the 5f6 and 5f7 electronic configurations Phys. Rev. B 28 2317

[170] Jin M, Guo Y, Li B, Niu X and Zhang Y 2018 Magnetic and electronic properties of α-U2N3 and its role in preventing uranium from oxidation: first-principles studies J. Nucl. Mater. 512 72–8

[171] Lawrence Bright E, Springell R, Porter D G, Collins S P and Lander G H 2019 Synchrontron x-ray scattering of magnetic and electronic structure of UN and U2N3 epitaxial films Phys. Rev. B 100 134426

[172] Shrestha K, Antonio D, Jaime M, Harrison N, Mast D S, Hamann S, Förster T, Gorbunov D I, König M, Uhlarz M, Aoki D, Maple MB, de Andrade MC, Herrmann J, Dickey RP, Dilley D G, Olsen C E and White R W 1965 Superconductivity of actinide systems J. Phys.: Condens. Matter 2 28

[173] Smith J L, Spirlet J C and Müller W 1979 Superconducting properties of protactinium Phys. Rev. Lett. 45 1860

[174] Smith J L and Haire R G 1966 Superconductivity of thorium and uranium Phys. Rev. 152 432

[175] Wolcott N M and Hein R A 1958 Superconductivity of thorium below 1 K Phil. Mag. 3 591–6

[176] Fowler R D, Matthews B T, Asprey L B, Hill H H, Lindsay J and Smith J Land Haire R G 1978 Superconductivity of americium Phys. Rev. 165 56

[177] Aschermann V G and Justi E 1942 Electrical conductivity, magnetic increase of resistance, Hall effect and superconductivity of rhenium Phys. Z. 43 207

[178] Goodman B B and Shoenberg D 1950 Superconductivity of uranium Nature 165 441–2

[179] Gordon J E, Montgomery H, Noer R J, Pickett G R and Tobón R 1966 Superconductivity of thorium and uranium Phys. Rev. 152 432

[180] Smith J L and Haire R G 1978 Superconductivity of americium Science 200 535–7

[181] Griveau J-C and Colineau E 2014 Superconductivity in transuranium elements and compounds C. R. Phys. 15 599–615

[182] Maple M B, de Andrade M C, Herrmann J, Dickey R P, Dilley N R and Han S 1997 Superconductivity in rare earth and actinide compounds J. Alloys Compd. 250 585–95

[183] Aoki D et al 2007 Unconventional heavy-fermion superconductivity of a new transuranium compound NpPd3Al2 J. Phys. Chem. Lett. 19 8188–94

[184] Griveau J-C, Gofryk K, Rebizant J and Dickey R P 2008 Transport and magnetic properties of the superconductor NpPd3Al2 Phys. Rev. B 77 212502

[185] Bauer E D et al 2011 Localized 5f electrons in superconducting PuCoIn3: consequences for superconductivity in PuCoGa3 J. Phys.: Condens. Matter 24 052206

[186] Wastin F, Boulet P, Rebizant J, Colineau E and Lander G H 2003 Advances in the preparation and characterization of transuranium systems J. Phys.: Condens. Matter 15 S2279

[187] Bauer E D and Thompson J D 2015 Plutonium-based heavy-fermion systems Annu. Rev. Condens. Matter Phys. 6 137–53

[188] Mydosh J A and Peter-Oppeneer M 2014 Hidden order behaviour in UNe2S12 (a critical review of the status of hidden order in 2014) Phil. Mag. 94 3642–62

[189] Mydosh J A, Peter-Oppeneer M and Riseborough P S 2020 Hidden order and beyond: an experimental–theoretical overview of the multifaceted behavior of UNe2S12 J. Phys.: Condens. Matter 32 143002

[190] Ott H R, Rudigier H, Fisk Z and Smith J L 1983 UBe13: an unconventional actinide superconductor Phys. Rev. Lett. 50 1595

[191] Ramshaw B J, Shekhter A, McDonald R D, Betts J B, Mitchell J N, Tobash P H, Mielke C H, Bauer E D and Migliori A 2015 Avoided valence transition in a plutonium superconductor Proc. Nail Acad. Sci. 111 3285–9

[192] Gofryk K, Griveau J-C, Riseborough P S and Durakiewicz T 2016 Thermoelectric power as a probe of density of states in correlated actinide materials: the case of PuCoGa3 superconductor Phys. Rev. B 94 195117

[193] Ran S et al 2019 Nearly ferromagnetic spin-triplet superconductivity Science 365 684–7

[194] Nakamine G et al 2019 Superconducting properties of heavy fermion UT2 revealed by 129Te-nuclear magnetic resonance J. Phys. Soc. Japan 88 113703

[195] Braithwaite D et al 2019 Multiple superconducting phases in a nearly ferromagnetic system Commun. Phys. 2 147

[196] Hayes I M et al 2020 Weyl superconductivity in UT2e (arXiv:2002.02539)

[197] Bae S et al 2021 Anomalous normal fluid response in a chiral superconductor UT2e Nat. Commun. 12 2644

[198] Bruin C, Cren T and Roditchev D 2016 Review of 2D superconductivity: the ultimate case of epitaxial monolayers Supercond. Sci. Technol. 30 013003

[199] Ostertag J P, Scheffler M, Dressel M and Jourdan M 2011 Terahertz conductivity of the heavy-fermion compound UNi2Al2 Phys. Rev. B 84 035132

[200] Bhardwaj V, Bhattacharya A, Varga L K, Ganguli A K and Chatterjee, R 2020 Thickness-dependent magneto-transport properties of topologically nontrivial DyPdBi thin films Nanotechnology 31 384001

[201] Cossard A, Desmarais J K, Casassa S, Gatti C and Erba A 2021 Charge density analysis of actinide compounds from the quantum theory of atoms in molecules and crystals J. Phys. Chem. Lett. 12 1862–8

[202] Richmond P and Sewell G L 1968 Electron correlations, magnetic ordering, and Mott insulation in solids J. Math. Phys. 7 349–56

[203] Krumrhim J, Mussen G, Borisova S, Stocia P, Plucinski L, Schneider C M and Grützmacher D 2011 MBE growth optimization of topological insulator Bi2Te3 films J. Cryst. Growth 324 1–8

[204] Krumrhim J, Mussen G, Borisova S, Stocia P, Plucinski L, Schneider C M and Grützmacher D 2011 MBE growth optimization of topological insulator Bi2Te3 films J. Cryst. Growth 324 1–8

[205] Ling F et al 2012 Quantum spin hall state in monolayer 1T'-WTe2 Nat. Phys. 9 123–8

[206] Hesjedal T 2019 Rare earth doping of topological insulators: a brief review of thin film and heterostructure systems Phys. Status Solidi A 216 1800726

[207] Ivanov V, Van X and Savrasov S Y 2019 Topological insulator-to-weyl semimetal transition in strongly correlated actinide system UNiSn Phys. Rev. X 9 041055

[208] Zhang X, Zhang H, Wang J, Felscher C and Zhang S-C 2012 Actinide topological insulator materials with strong interaction Science 335 1464–6

[209] Choi HW et al 2018 Experimental and theoretical study of topology and electronic correlations in PuB2 Phys. Rev. B 97 201114

[210] D’Agnardi A P et al 2019 239Pu nuclear magnetic resonance in the candidate topological insulator PuB2 Phys. Rev. B 99 035104

[211] Deng X, Haule K and Kotliar G 2013 Plutonium hexaboride is a correlated topological insulator Phys. Rev. Lett. 111 176404
[212] Dzero M, Sun K, Galitski V and Coleman, P 2010 Topological Kondo insulators Phys. Rev. Lett. 104 106408
[213] Kohn W and Sham L J 1965 Self-consistent equations including exchange and correlation effects Phys. Rev. 140 1133
[214] Hohenberg P and Kohn W 1964 Inhomogeneous electron gas Phys. Rev. 136 864
[215] Burke K 2012 Perspective on density functional theory J. Chem. Phys. 136 150901
[216] Jones R O 2015 Density functional theory: its origins, rise to prominence, and future Rev. Mod. Phys. 87 897
[217] Cramer C J and Truhlar D G 2009 Density functional theory calculations for quantum impurity models and Werner. Phys. Rev. B 123 041401
[218] Haule K 2007 Quantum Monte Carlo impurity solver for clusters Phys. Chem. Chem. Phys. 11 10757
[219] Hasnip P J, Refson K, Probert M, Yates J R, Clark S J and Pickard C J 2014 Density functional theory in the solid state Phil. Trans. R. Soc. A 372 20130270
[220] Jain A, Shin Y and Persson K A 2016 Computational predictions of energy materials using density functional theory Nat. Rev. Mater. 1 15004
[221] Maurer R J, Freysoldt C, Reilly A M, Brandenburg J G, Hofmann O T, Bjorkman T, Lebegue S and Tkatchenko A 2019 Advances in density-functional calculations for materials modeling Annu. Rev. Mater. Res. 49 1
[222] Perdew J P and Schmidt K 2001 Jacob’s ladder of density functional approximations for the exchange–correlation energy Density Functional Theory and Its Application to Materials, AIP Conference Proceedings (Antwerp, Belgium – 8–10 June 2000) vol 577 ed V Van Doren, C Van Alsenoy and P Geerlings
[223] Kotliar G, Savrasov S Y, Haule K, Oudovenko V S, Parcollet O and Marianetti C A 2006 Electronic structure calculations with dynamical mean-field theory Rev. Mod. Phys. 78 865
[224] Cohen A J, Mori-Sanchez P and Yang W T 2008 Insights into current limitations of density functional theory Science 321 792
[225] Imada M, Fujimori A and Tokura Y 1998 Metal–insulator transitions Rev. Mod. Phys. 70 1039
[226] Perdew J P et al 2017 Understanding band gaps of solids in generalized Kohn–Sham theory Proc. Natl Acad. Sci. USA 114 2801
[227] Georges A, Kotliar G, Krauth W and Rozenberg M J 1996 Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions Rev. Mod. Phys. 68 13
[228] Werner P, Comanac A, Medici L D, Troyer M and Millis A J 2006 Continuous-time solver for quantum impurity models Phys. Rev. Lett. 97 076405
[229] Haule K 2007 Quantum Monte Carlo impurity solver for cluster dynamical mean-field theory and electronic structure calculations with adjustable cluster base Phys. Rev. B 75 155113
[230] Muller A J, Lichtenstein A I, Rubtsov A N, Troyer M and Werner. P 2011 Continuous-time Monte-Carlo methods for quantum impurity models Rev. Mod. Phys. 83 349
[231] Marianetti C A, Haule K, Kotliar G and Fluss M J 2008 Electronic coherence in delta-Pt; a dynamical mean-field theory study Phys. Rev. Lett. 101 056403
[232] Park H, Millis A J and Marianetti C A 2014 Total energy calculations using DFT plus DMFT: computing the pressure phase diagram of the rare earth nickelates Phys. Rev. B 89 245133
[233] Isaacs E B and Marianetti C A 2020 Compositional phase stability of correlated electron materials within DFT + DMFT Phys. Rev. B 102 045146
[234] Adler R, Kang C J, Yee C H and Kotliar G 2019 Correlated materials design: prospects and challenges Rep. Prog. Phys. 82 012504
[235] Chakraborti B, Birol T and Haule K 2017 Role of entropy and structural parameters in the spin-state transition of LaCoO3 Phys. Rev. Mater. 1 064403
[236] Lechermann F 2020 Multiorbital processes rule the Nd1−xSr2xO3 normal state Phys. Rev. X 10 041002
[237] Anisimov V I, Aryasetiawan F and Lichtenstein A I 1997 First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA + U method J. Phys.: Condens. Matter 9 767
[238] Sahoo B D, Joshi K D and Kauschik T C 2020 Structural, elastic, vibrational, thermophysical properties and pressure-induced phase transitions of ThN2, ThN3, and Th2N2: an ab initio investigation J. Appl. Phys. 128 035902
[239] Adachi J, Kurosaki K, Uno M and Yamanaoka S 2005 A molecular dynamics study of thorium nitride J. Alloys Compd. 394 312–6
[240] Attia-Fynn R and Ray A K 2007 Density functional study of the actinide nitrides Phys. Rev. B 76 115101
[241] Reyren N et al 2007 Superconducting interfaces between insulating oxides Science 317 1196
[242] Di Castro D, Cantoni C, Ridolfi F, Aruta C, Tebano A, Yang N and Balestrino G 2015 High-Tc superconductivity at the interface between the CaCuO2 and SrTiO3 insulating oxides Phys. Rev. Lett. 115 147001
[243] Luders U, Sheets W C, David A, Pellier W and Frensard R 2009 Room-temperature magnetism in LaV03/SrVO3 superlattices by geometrically confined doping Phys. Rev. B 80 241102
[244] Boris A V et al 2011 Dimensionality control of electronic phase transitions in nickel-oxide superlattices Science 332 937
[245] Chakhalian, Freeland J W, Habermeier H U, Cristiani G, Khaliullin G, VanVeenendaal M and Keimer B 2007 Orbital reconstruction and covalent bonding at an oxide interface Science 318 1114
[246] Bibes M, Villegas J E and Barthelemy A 2011 Ultrathin oxide films and interfaces for electronics and spintronics Adv. Mater. 60 5
[247] Chen H H, Millis A J and Marianetti C A 2013 Engineering correlation effects via artificially designed oxide superlattices Phys. Rev. Lett. 111 116403
[248] Zhong Z C, Wallerberger M, Tomczak J M, Taranto C, Parragh N, Toschi A, Sangiovanni G and Held K 2015 Electronics with correlated oxides: SrV03/SrTiO3 as a Mott transistor Phys. Rev. Lett. 114 246401
[249] James A D N, Aichhorn M and Laverock J 2021 Quantum confinement induced metal–insulator transition in strongly correlated quantum wells of SrV03 superlattices Phys. Rev. Res. 3 023149
[250] Gao D and Ray A K 2006 On the convergence of the electronic structure properties of the fcc americium (0 0 1) surface Surf. Sci. 600 4941–52
[251] Gao D and Ray A K 2008 Relativistic density functional study of fcc americium and the (111) surface Phys. Rev. B 77 035123
[252] Sikorski E L, Jaques B J and Li, L 2021 First-principles magnetic treatment of the uranium nitride (100) surface and effect on corrosion initiation J. Appl. Phys. 130 095301
[253] Kroemer H 2001 Quasi-electric fields and band offsets: teaching electrons new tricks (nobel lecture) ChemPhysChem 2 490–9
[254] Bennett C A, Poudel N, Simmonds P J, Tiwari A, Hurley D H and Gofryk K 2022 Towards actinide heterostructure synthesis and science Nat. Commun. 13 2221
[255] Block M, Lalitaiou M and Raeder S 2021 Recent progress in laser spectroscopy of the actinides Prog. Part. Nucl. Phys. 116 103834
[255] Grover P, Ferch L S and Schreckenbach G 2020 Adsorption of actinide (U–Pu) complexes on the silicene and germanene surface: a theoretical study J. Phys. Chem. A 124 1522–34

[256] Lopez-Bezanilla A 2020 f-orbital based Dirac states in a two-dimensional uranium compound J. Phys. Mater. 3 024002

[257] Park S-J and Seo M-K 2011 Interface Science and Composites 1st edn (Amsterdam: Elsevier) p 852

[258] Murali S, Zhang C, Goryll M, King R R and Honsberg C B 2020 Study of pit formation in MBE grown GaP on misoriented Si J. Vac. Sci. Technol. B 38 032201

[259] Simon J, Tomasulo S, Simmonds P J, Romero M and Lee M L 2011 Metamorphic gasp buffers for growth of wide-bandgap inga cells J. Appl. Phys. 109 013708

[260] Benyahia D, Kubiszyn Ł, Michalczewski K, Kęblowski A, Martyniuk P and , Piotrowski J A R et al 2018 Optimization of the interfacial misfit array growth mode of GaSb epilayers on GaAs substrate J. Cryst. Growth 483 26–30

[261] Sautter K E, Vallejo K D and Simmonds P J 2020 Strain-driven quantum dot self-assembly by molecular beam epitaxy J. Appl. Phys. 128 031101

[262] Makimoto T, Kumakura K, Maeda M, Yamamoto H and Horikoshi Y 2015 A new AlN buffer layer for RF-MBE growth of AlN on a sapphire substrate J. Cryst. Growth 425 138–40

[263] Vallejo K D, Garrett T A, Cabrera C I, Liang B, Grossklaus K A and Simmonds P J 2021 Tensile-strained self-assembly of InGaAs on InAs(111)A J. Vac. Sci. Technol. B 39 062809

[264] He X et al 2021 Step-graded AlGaN vs superlattice: role of strain relief layer in dynamic on-resistance degradation Appl. Phys. Express 15 011001

[265] Nandi U, Mohammadi M, Lu H, Norman J, Gossard A C, Alff L and Preu S 2021 Material properties and performance of ErAs: in (Al)GaAs photoconductors for 1550 nm laser operation J. Vac. Sci. Technol. A 39 023407

[266] Jin P, Ye X L and Wang Z G 2005 Growth of low-density InAs/GaAs quantum dots on a substrate with an intentional temperature gradient by molecular beam epitaxy Nanotechnology 16 2775

[267] Matthews J W and Blakeslee A E 1974 Defects in epitaxial multilayers: I. Misfit dislocations J. Cryst. Growth 27 118–25

[268] Rough F A and Bauer A A 1958 Constitution of uranium and thorium alloys Technical Report (Columbus, Ohio: Battelle Memorial Inst.)