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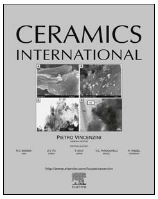

Electrochemical synthesis and characterization of erbium oxide

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ABSTRACT

Erbium oxide (Er_2O_3) has been used in a variety of microelectronic, optoelectronic, thermophotovoltaic, and biomedical applications, and especially in nuclear reactor systems. Electrochemical synthesis of rare earth oxides has conventionally been based upon base generation under the application of anodic or cathodic potential and subsequent sintering of as-deposited rare earth hydroxides. In this study, we investigated a direct, room-temperature electrochemical synthesis of Er_2O_3 onto titanium base metal by applying cathodic potentials. Iminodiacetate (IDA) ligand was added to form $Er(IDA)_2^-$ complexes with Er^{3+} in a neutral electrolyte. A cathodic reaction for the direct deposition of Er_2O_3 from $Er(IDA)_2^-$ was suggested as the mechanism of Er_2O_3 synthesis. The formation of cubic Er_2O_3 phase at all applied potentials was verified by means of X-ray diffractometry and X-ray photoelectron spectroscopy. The relationship between the diffusion characteristics of the reacting ions and the resulting microstructures of Er_2O_3 deposits was also studied as a function of applied potential.

1. Introduction

Er_2O_3 has been used for gate dielectrics of silicon-based microelectronic devices due to its high dielectric constant [1–3]. It also has attracted attention for optoelectronic applications because it emits light of specific wavelengths [4,5]. In solar cells, Er_2O_3 films could be used as anti-reflection coatings [6]. So far, the formation of Er_2O_3 on substrates has been carried out mostly by means of vacuum techniques such as magnetron sputtering, electron beam evaporation, metalorganic chemical vapor deposition, and atomic layer deposition. Besides these techniques, laser heating synthesis has been used to prepare polycrystalline Er_2O_3 for thermophotovoltaic generators [7]. Erbia (cubic Er_2O_3) with excellent chemical and thermal stability at high temperatures has been used as a selective emitter for thermophotovoltaic systems in the field of hypersonic aerodynamics [8,9]. In liquid lithium blanket systems, Er_2O_3 as an insulting coating has been effective in reducing magnetohydrodynamic pressure drop [10].

Over the last decade, Er_2O_3 has been intensively studied as a tritium or deuterium (hydrogen) permeation barrier for nuclear reactors [11–13]. Filtered arc deposition has been the method most commonly used to deposit an Er_2O_3 barrier onto a base metal, typically steel, although some researchers have demonstrated the formation of Er_2O_3 by means of sol-gel methods [14,15]. In other research, nickel and titanium have been proposed as alternative base metals to steel, and the coating of rare earth oxides including Er_2O_3 as hydrogen permeation barriers on these metals has been demonstrated [16]. There are two requirements for any method for depositing Er_2O_3 as a hydrogen permeation barrier for use in a nuclear reactor: low-temperature processing and plant-scale deposition ability [11]. Electrochemical deposition could satisfy these requirements, and additionally would be suitable for the economical formation of an Er_2O_3 barrier on a base metal substrate by means of a continuous process. Another advantage of electrochemical deposition is that it could be used to synthesize an Er_2O_3 barrier on both sides of a base metal substrate simultaneously.

Despite the potential merits of electrochemical Er_2O_3 deposition, it has not been reported previously, likely owing to the following difficulties. First, the redox potential of Er_2O_3 is so negative that H_2 gas generation is highly preferred over Er_2O_3 deposition in aqueous solution. Moreover, Er_2O_3 is not stable even in the anodic and alkaline region of the Pourbaix diagram of the erbium–water system [17]. The electrochemical synthesis of rare earth oxides is well known to be difficult, with the exception of PrO_2, NdO_2, CeO_2, and TbO_2, which can be theoretically electroformed by means of anodic deposition in alkaline solutions [18]. Among these exceptional rare earth oxides, anodic or cathodic electrodeposition of CeO_2 has been most frequently studied together with subsequent sintering of electrodeposited $Ce(OH)_3$ [19–21]. In this process, $Ce(OH)_3$ is initially electrodeposited along with base generation, and is then sintered to transform it into CeO_2. In addition, some researchers have reported that Sm_2O_3 and Gd_2O_3 could be electrochemically synthesized by means of base generation and sintering,

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similar to the electrochemical deposition of CeO_2, even though their electrodeposition is not available theoretically [22–24].

In this study, we investigated the direct electrochemical synthesis of Er_2O_3 film on titanium substrate in neutral aqueous solution at room temperature. Unlike most previous reports regarding the electrochemical synthesis of rare earth oxides, which included in common the initial formation of rare earth hydroxides, we deposited Er_2O_3 directly onto titanium by means of one-step cathodic electrodeposition from a neutral solution including iminodiacetate (IDA) as a complexing agent. We suggest a mechanism for the electrodeposition of Er_2O_3 onto titanium, based upon simple thermodynamic calculations. The formation of Er_2O_3 phase was ascertained by means of X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental procedure

A three-electrode electrochemical cell was prepared, including a potentiostat (G750, Gamry Instruments) that was used to apply cathodic potentials for electrochemical deposition while simultaneously acquiring electrochemical characteristic curves. Titanium foil substrate of $20 \times 20 \times 0.1$ mm^3 was used as a working electrode and a platinum mesh was used as a counter electrode. Prior to electrodeposition, each titanium substrate specimen was cleaned by dipping it in dilute nitric acid and ethanol and then treating it in an ultrasonic cleaner. All potential values reported in this study were measured with respect to an Ag/AgCl reference electrode. To characterize the influence of Er^{3+} and IDA upon cathodic reduction, cathodic cyclic voltammetry (CV) was conducted in the potential range of 0 to -4.0 V at the scan rate of 5 mV s^{-1}. Growth of Er_2O_3 on titanium was conducted for 60 s at room temperature while applying the constant cathodic potential of either -2.5, -3.0, -3.5, or -4.0 V.

A neutral aqueous solution composed of $ErCl_3 \cdot H_2O$ (0.1 M), H_2IDA ($C_4H_7NO_4$; iminodiacetic acid; 1 M), HCl (10 ppm), and KOH for pH control was used as an electrolyte. This electrolyte had an Er^{3+}:IDA ligand concentration ratio of 1:10 to ensure diffusion-limited reduction conditions during the cathodic electrodeposition. The diffusion characteristics of the reducing ions were evaluated at each applied potential by converting current transient (*I*–*t*) curves to I–$t^{-1/2}$ curves, according to the Cottrell equation.

An X-ray diffractometer (D/MAXIIIC, Rigaku) was used to identify the crystalline phase of erbium-based deposits grown on titanium. Detailed characterization of erbium-based deposits was carried out by means of X-ray photoelectron spectrometry (K-Alpha, Thermo Scientific). XPS analysis also included 1-μm depth profiling of major elements in an erbium-based deposit electrodeposited at -4.0 V. Field emission scanning electron microscopy (FE-SEM, Quanta 200, FEI) was conducted to acquire surface morphological images of erbium-based deposits fabricated under various applied potentials.

3. Results and discussion

CV traces were collected for aqueous Er^{3+}, IDA, and Er^{3+}/IDA solutions, including cathodic potential scanning up to -4.0 V at the scan rate of 5 mV s^{-1} (Fig. 1). Although the Er^{3+}/IDA solution was selected as the electrolyte for direct electrochemical deposition of Er_2O_3 onto titanium, the Er^{3+} solution and IDA solution were studied to understand cathodic reactions in these solutions as a means to understand the chelation of IDA with Er^{3+}. In the IDA solution, the reduction current evolved from about -1.0 V and increased almost linearly with further negative potential shift. H_2 gas was consistently generated on the titanium surface during cathodic CV in the IDA solution, but no deposit was found. In the Er^{3+} solution, a linear increase of reduction current similar to that in the IDA solution was observed, except that reduction began at a cathodic potential shifted negatively by 0.2 V; also similarly, H_2 gas evolution was the only reduction process observed. Theoretically, Er^{3+} ions can be reduced to Er metal on titanium under large cathodic potentials. For [Er^{3+}] of 0.1 M in the Er^{3+} solution, the redox potential of the reaction $Er^{3+} + 3e^- \leftrightarrow Er$ can be calculated as -2.513 V versus Ag/AgCl. However, no local reduction peak in the CV plot and no solid deposit on the titanium surface were observed during the cathodic potential scan of the Er^{3+} solution. Instead, when the pH of the 0.1 M Er^{3+} solution was increased to 7, a pink, powdery precipitate of Er_2O_3 sank to the bottom of the solution; this precipitate formed according to the following equilibrium reaction (1).

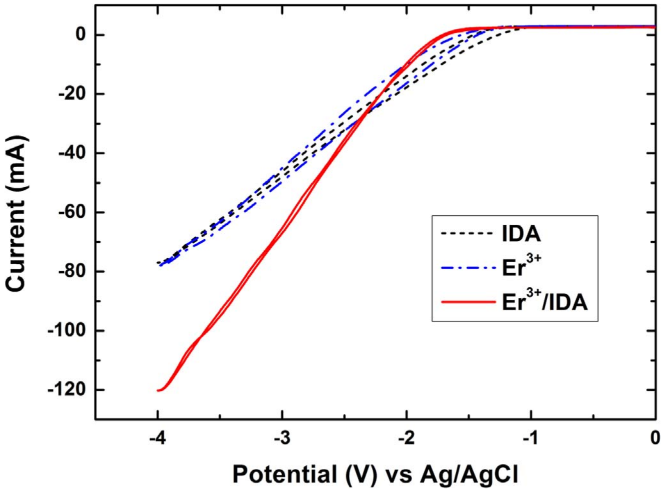

Fig. 1. Cyclic voltammograms of the Er^{3+}, IDA, and Er^{3+}/IDA solutions in cathodic region using a titanium working electrode. Its scan rate is 5 mV/s.

$$2\,Er^{3+}(aq) + 3H_2O(l) \leftrightarrow Er_2O_3(s) + 6H^+(aq) \tag{1}$$

$$\log[Er^{3+}] = 19 \cdot 70\text{–}3\ pH \tag{2}$$

Reaction (2) can be built based upon reaction (1) to calculate the equilibrium concentration of Er^{3+} ions in water [17]. At pH 7, the equilibrium concentration of Er^{3+} is 0.05 M. Er^{3+} ions of 0.1 M existed in the Er^{3+} solution used in this study; thus, reaction (1) would proceed in the right direction, producing Er_2O_3 precipitate until a [Er^{3+}] of 0.05 M was reached.

However, no precipitation of Er_2O_3 was observed in the Er^{3+}/IDA solution at pH 7. We assume that most Er^{3+} ions prefer to form complexes with IDA ligands instead of following reaction (1) in the right direction, which would yield a concentration of free Er^{3+} ions less than 0.05 M. To verify this assumption, it is necessary to identify the type and concentration of IDA ligands chelating Er^{3+} ions and to calculate the concentrations of both Er–IDA complexes and free Er^{3+} ions.

Ionization of H_2IDA as a diprotic acid happens through two steps of single proton loss, as below.

$$H_2IDA(aq) \leftrightarrow HIDA^-(aq) + H^+(aq) \tag{3}$$

$$K_{a1} = \frac{[HIDA^-][H^+]}{[H_2IDA]};\ pK_{a1} = 2.58 \tag{4}$$

$$HIDA^-(aq) \leftrightarrow IDA^{2-}(aq) + H^+(aq) \tag{5}$$