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CVD Lu₂O₃:Eu coatings For Advanced Scintillators

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Abstract

Currently Lu₂O₃:Eu³⁺ scintillators can only be fabricated via hot-pressing and pixelization, which is commercially not viable, thus restricting their use. Chemical vapor deposition is being developed as an alternative manufacturing process. Columnar coatings of Lu₂O₃:Eu³⁺ have been achieved using the halide-CO₂-H₂ system, clearly signifying feasibility of the CVD process. Characterization of the coatings using high resolution scanning electron microscopy (SEM) and x-ray diffraction (XRD) analysis have been used as an aid to optimize process parameters and attain highly oriented and engineered coating structures. These results have clearly demonstrated that this process can be successfully used to tailor sub-micron columnar growth of Lu₂O₃:Eu³⁺, with the potential of ultra high resolution x-ray imaging.

Keywords

Chemical vapor deposition; Scintillators; Luminescence

Introduction

Extensive research has been performed on the development of scintillating materials with improved physical and emissive properties [1,2]. Many different materials, ranging from organic polymers to inorganic oxides and halides have been developed, each demonstrating unique characteristics [3]. Europium-doped lutetium oxide (Lu₂O₃:Eu³⁺) has demonstrated great promise as an alternative to both the industry standards; bismuth orthogermanate (BGO) and thallium doped cesium iodide (CsI:Tl) [3–5].

Lutetium oxide has an extremely high density of 9.4 g/cc and a high radiation resistance makes it a great candidate for high energy applications for which BGO is currently the standard [2]. However, BGO has a lower density of 7.13 g/cc and emits less than 10 photons/keV [3,4]. Moreover, Lu₂O₃:Eu³⁺ has a high luminescent efficiency of 30 photons/keV, making it excellent for diagnostic imaging for which CsI:Tl is currently the standard [1,2]. Although CsI:Tl has a high emission of 60 photons/keV, it suffers from radiation damage at high doses, it is slightly hygroscopic and has a low density of 4.51 g/cc [3,5,6].

The use of lutetium oxide has been limited due to its high melting temperature (2490°C) that makes fabrication of single crystals commercially unviable. Consequently, processes have recently been developed for fabricating transparent Lu₂O₃ by hot pressing or sintering [1,2, 7]. While such processes do result in high quality transparent material, both economic and technical considerations have restricted its application to small detectors. Furthermore, hot

pressed or sintered Lu_2O_3 needs to be physically subdivided into individual pixels [2] (Fig. 1 (a)), each coated to minimize optical cross-talk. All these post-processes are extremely labor intensive and expensive.

The present industry standard, CsI:Tl has a low melting temperature and thus can be easily fabricated into a single crystal or by vapor deposition into a columnar structure [2] as shown in Fig. 1(b). Such a columnar structure has an optical fiber effect by internally reflecting emitted light and does not require the post processing to eliminate cross-talk. This investigation was undertaken to develop a vapor deposition process, to co-deposit europium doped lutetium oxide coatings, directly producing a custom structured scintillator capable of high-resolution imaging. It is expected that this would result in a more economical and commercially viable process minus the expensive post-fabrication steps.

Vapor Deposition

Broadly, vapor deposition can be divided into physical vapor deposition (PVD) by which CsI:Tl is deposited, and chemical vapor deposition (CVD). Since the development of PVD of europium doped lutetium oxide coatings have been previously reported [8], the current study focuses on the CVD process.

CVD of films and coatings involve the chemical reactions of gaseous reactants on or near the vicinity of a heated substrate surface. This atomistic deposition method can provide high purity materials with structural control at atomic or nanometer scale level. Moreover, it can produce single layer, multilayer, composite, nanostructured, and functionally graded coating materials with well controlled dimension and unique structure at low processing temperatures [9]. Furthermore, one of the unique features of CVD over other deposition techniques is the non-line-of-sight-deposition capability that has allowed the coating of complex shaped components.

In addition, CVD can be carried out employing hot or cold wall reactors. In hot wall CVD, the deposition chamber is heated which in turn heats the gases through conduction and radiation. Though the hot wall reactor can provide very precise temperature control, the interior of the hot wall reactor is also coated (heterogeneous nucleation) and can induce gas phase (homogeneous) nucleation, resulting in maintenance problems and lower deposition efficiency [10]. In addition, depletion of gaseous reactants also occurs along the reactor requiring complex systems for large substrates [11].

In a cold wall reactor only the substrate is heated, either inductively or resistively, and the wall of the reactor is cold. Most of the CVD reactions are endothermic. Therefore, the deposition reaction will occur only on the heated substrate, and negligible deposition on the wall of the reactor. Although these reactors are more complex, they allow greater control over the deposition process, enabling higher quality coatings. However, thermal convection, which occurs in a cold wall reactor, can create concentration gradients of the reactive species and result in non-uniform coatings. This limitation can be overcome by performing the CVD cold wall deposition at a reduced pressure [10,11]. Factors which determine the heating method are the size and geometry of the substrate, and whether it is conducting or non-conducting. Additionally, by using cold wall CVD and thus avoiding homogeneous nucleation, higher growth rates can be achieved. This drastically reduces the deposition time to achieve thick coatings necessary to absorb most of the incident radiation.

The analysis of the CVD processes includes the understanding of the (a) thermodynamics, (b) chemical kinetics and (c) mass transport phenomena. An understanding of the parameters can lead to the control of the structure, stoichiometry, crystallinity and texture of films [10,11].

Experimental

Many CVD processes use the metal chloride-H₂-CO₂ system [9–12]. In this study, thermodynamic calculations using HSC™ were used to determine the viability of the CVD process. The hypothesized deposition reaction equation for Lu₂O₃:Eu³⁺ as shown in Eq. 1 was made using a combination of two individual Eq. 2 and 3.

The Gibbs free energy of reaction for Eq. 2 is −439 kJ/mol as opposed to a value of −170 kJ/mol for Eq. 3 at 1000°C. Although this difference in free energy could result in a variance between deposit and gas composition, it is favorable in this study as low amounts of Eu are desired in the coating deposits.

Even though LuCl₃ and EuCl₃ are solids at room temperature, their vapor pressure at deposition temperatures (1000°C) are high enough to provide an adequate reactant flow. Since the chlorides are extremely hygroscopic, they were generated in-situ by reacting lutetium and europium metal with judicious control of the temperature and the chlorine flow rates.

It has been established that a europium concentration of 5–7 mol% in the Lu₂O₃:Eu³⁺ system yields the highest emission intensity [1,2]. Furthermore, the ability to interpret an image is directly related to the emission intensity uniformity and thus dopant uniformity is essential to the imaging process. With knowledge of the variance in free energy of formation of Lu₂O₃ and Eu₂O₃, the ratio of Lu and Eu in the internal chloride generator was empirically determined in order to achieve the desirable level of Eu doping. To maintain 5–7 mol% Eu in the deposit, both the metals were uniformly mixed to avoid excess preferential reactions. Europium chloride melts above 730°C and although lutetium chloride melts at 925°C, it sublimates above 750°C. By combining elevated temperatures and low pressure, it is possible to ensure the metal-chlorine reaction to be the limiting kinetics and not evaporation/sublimation, thus providing the necessary control.

The cold wall CVD uses a radio frequency (RF) induction heater to heat the substrate and crucible using graphite susceptors. The reactants used for deposition were metal chlorides, CO₂, H₂ and Argon as a dilutant. Excess H₂ was present to ensure complete reduction of metal chlorides. Process parameters range from 950°C to 1050°C for both the substrate and the generator, between 50 and 150 mbar, and with a total flow rate of approximately 2 slm. Morphological analysis of the coatings was performed using a Zeiss VP40 high resolution scanning electron microscope (SEM) in conjunction with a Bruker D8 Focus X-ray diffractometer (XRD) in $\theta/2\theta$ mode. Emission properties were confirmed using a Gatan MonoCL2 cathodoluminescence spectrometer.

Results and Discussion

Since many parameters affect the coating structure and properties, various configurations were designed and tested. One of the problems encountered was the formation of metal oxy-chlorides due to a high metal chloride partial pressure and short mixing times. This was resolved by maintaining a minimal distance between the substrate and the gas outlet to allow for proper mixing and by supplying sufficient CO_2 and H_2 to fully reduce the metal chlorides.

Such a set-up configuration led to the deposition of coatings in a columnar fashion with a strong orientation preference growth directly from the first nucleated, equiaxed layer deposited on the substrate. Such microstructure is a result of high supersaturation and limited lateral diffusion. This structure is desirable for radiation detection since every column would act as one 'pixel'.

When grown at approximately 1000°C on an amorphous quartz substrate with a growth rate of approximately $3.2\mu\text{m/hr}$, a columnar structure emerged as seen in Fig. 2. The columnar grains appear to have an average diameter of approximately $1.5\mu\text{m}$ and a total coating thickness of approximately $6.4\mu\text{m}$. When comparing the XRD plot in Fig. 3(a) to a polycrystalline powder diffraction plot in Fig. 3(b), a clear (100) orientation preference is visible. Such a preference for the (100) orientation indicates a free energy minimization for growth in this direction. Observations of the surface morphology in Fig. 2(b) revealed the columnar growth to consist of stacked platelets or discs growing perpendicular to the (100) direction. Such a layer to layer formation has been defined as Frank-van der Merwe (FM) growth and typically leads to smooth surfaces [13].

Growth conditions were then modified by decreasing the ratio of metal chloride to unreacted chlorine whilst keeping the total chlorine flow rate constant. This led to the deposition of a highly faceted columnar structure, as seen in Fig. 4, with a growth rate of $0.5\mu\text{m/hr}$ and a coating thickness approximately $2.4\mu\text{m}$. The columnar growth appears to be single grained, with an average diameter of approximately 450nm and with a clear surface morphology. This could be indicative of either a cellular or dendritic growth or simply a surface effect. This type of growth has been referred to Volmer-Weber (VW) and typically leads to rough surfaces [13]. The XRD plot in Fig. 5 combined with the SEM images in Fig. 4 show the preferred orientation to be in the (100) direction, perpendicular to the substrate surface. The effect of the columnar wall features on the optical properties is difficult to determine. However, these are most likely not conducive to internal reflections to create an optical fiber effect. The ability to drastically tailor morphology, and size of the columnar grains via CVD processing parameters, is exciting, since it can be beneficially used to engineer coatings to fit specific applications.

Emission properties

Both lutetium and europium oxide have similar body center cubic (BCC) lattice ($\text{Lu}_2\text{O}_3 = 10.39\text{\AA}$, $\text{Eu}_2\text{O}_3 = 10.87\text{\AA}$) and form a complete solid solution. For optimal emission to occur, europium must form a solid solution by substituting into the lutetium site of Lu_2O_3 as Eu^{+3} . Although lutetium has only one stable oxidation state of +3, meaning it can only exist as Lu_2O_3 , europium can have either +2 or +3, creating structures such as EuO , Eu_2O_3 , Eu_3O_4 and potentially more. Thermodynamically, Eu_2O_3 is significantly more favorable, however, it is possible to deposit non-equilibrium phases in CVD. Experimental results confirmed this possibility when solely depositing europium yielded europium monoxide (EuO). It was hypothesized that as a result of the co-deposition, the europium would be forced into the +3 valence. Furthermore, it is possible for europium oxide to form a second phase rather than go into solution which would result in non-optimal emission. This was visible in certain circumstances where a second phase of Eu_2O_3 was visible in the XRD plots, proving the formation of a solid solution to be difficult. However, XRD plot in Fig. 5 shows no second

phase and the emission spectrum in Fig. 6 confirmed europium to be in the correct valence, proving that a solid solution has been achieved. If Eu^{2+} were present, there would be a broad emission peak from 400 to 500nm, however, only Eu^{3+} is visible, which has many peaks and the standard maximum intensity peak at 611nm, which corresponds to the ${}^5\text{D}_0 - {}^7\text{F}_2$ transition [1,2,14].

Conclusion

A process was developed to grow highly oriented columnar optical coatings using a cold wall CVD process. Promising results have proven the possibility of creating a coating that can combine the optimal emissive properties of single crystals with fiber optic columnar properties. Such a process would enable production of large area high quality transparent optical coatings and reduce manufacturing times by removing post processing steps. Future work will include production of 200-micrometer coatings that can be properly analyzed and compared to a pixelized ceramic.

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Fig. 1.
(a) Lu_2O_3 transparent ceramic pixelized by laser ablation [2]. (b) Commercially produced columnar CsI:Tl courtesy of Radiation Monitoring Devices, Inc. [2].

Fig. 2.
SEM micrographs of the stacked platelet columnar growth (a) Fractured cross section (b) Top surface.

Fig. 3.

(a) XRD plot of the stacked platelet columnar coating with indexed key peaks labeled. (b) Reference XRD plot for single phase polycrystalline lutetium oxide powder doped with 5 mol % europium oxide with indexed key peaks.

Fig. 4.
SEM micrographs of highly faceted columnar growth (a) Fractured cross section (b) Top surface.

Fig. 5.
XRD plot of the highly faceted columnar coating with indexed key peaks.

Fig. 6. Cathodoluminescence spectrum for the highly faceted coating with peak emission at 611 nm, corresponding to Eu^{3+} . Various emissions have been labeled.