Mini Review

Using the USP Technique and White Light Generation

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Abstract

This work presents a comprehensive overview of white light generation from oxide-based thin films synthesized by the ultrasonic spray pyrolysis (USP) technique, highlighting its versatility, scalability and suitability for solid-state lighting applications. A range of aluminium-, hafnium- and zinc-based oxide coatings, either undoped or selectively doped and co-doped with rare-earth (Ce^{3+}, Tb^{3+}, Eu^{3+}, Dy^{3+}) and transition-metal (Mn^{2+}) ions, were systematically investigated with respect to their luminescent properties. Depending on the host matrix, dopant combination and excitation conditions, emissions spanning the entire visible spectrum were achieved. White light generation was obtained through different strategies; intrinsic broadband emission of the host lattice, superposition of individual rare- earth emissions in single or multilayer architectures, and efficient non-radiative energy transfer processes sensitized by Ce^{3+} ions. Chromaticity coordinates obtained for several optimized coatings lie close to the ideal white point, with correlated colour temperatures ranging from warm to cold white, depending on dopant chemistry and concentration. Structural analyses reveal that both crystalline and amorphous matrices can support efficient luminescence, while cathodoluminescence studies further demonstrate the suitability of these films for advanced photonic applications. Overall, the results establish USP as a powerful and flexible deposition technique for engineering oxide thin-film phosphors with tunable white light emission. The demonstrated combination of optical quality, compositional flexibility and efficient energy transfer positions these materials as strong candidates for next-generation white light sources in solid-state lighting and display technologies.

Introduction

The growing interest in materials in the form of thin films or coatings has led to a substantial diversification of preparation methods. Thin films have become essential components in a wide range of applications, particularly in optics and optoelectronics, and their role in modern technology is now well established. Consequently, the synthesis of these materials has stimulated the development of numerous deposition processes, each characterized by specific advantages and limitations in terms of implementation complexity and the quality of the resulting deposit.

At present, many techniques are available for the preparation of thin films, which may be broadly classified into two main groups: Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD). CVD involves a heterogeneous chemical reaction in the gas phase at the surface of a substrate and does not necessarily require the use of high vacuum conditions [1]. Within this category lies the ultrasonic spray pyrolysis (USP) technique. This method was developed by the research group at the Grenoble Nuclear Research Centre (CENG) and patented in 1971 under the name “Pyrosol Process”. Owing to its versatility, this technique has been widely employed worldwide to produce

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materials in the form of thin films and ultrafine powders exhibiting magnetic, optical, semiconducting or superconducting properties [2]. In this review, selected results obtained from thin films and coatings prepared using the ultrasonic spray pyrolysis (USP) technique are presented. Emphasis is placed on systems in which photoluminescent properties have been successfully achieved, highlighting the potential of USP as a versatile and effective route for the fabrication of functional photoluminescent materials.

The USP technique is frequently used for thin film growth and powder preparation. This technique is suitable for depositing films that require large areas at low cost, thanks to its easy integration into industrial settings. Moreover, the technique is straightforward to operate, as it does not require sophisticated vacuum systems, while still yielding materials of excellent quality. It has been successfully employed for the deposition of a wide range of thin films, including oxides, sulphides and metals, as well as rare-earth-doped materials [3,4]. The method is based on the atomization of a chemical solution, which is directed towards a heated substrate where the pyrolytic reaction takes place.

Spray pyrolysis can be classified into two main variants: Pneumatically Generated Spray Pyrolysis [3] and Ultrasonically Generated Spray Pyrolysis (USP). In the present review, particular emphasis is placed on the USP technique [2].

It is widely recognized that the droplet size produced by an ultrasonic generator (piezoelectric transducer) plays a critical role in determining film quality. Improved results are obtained by controlling the intensity of ultrasonic agitation used to generate the aerosol. This approach enables the fabrication of homogeneous thin films exhibiting high-quality properties, such as good adhesion and chemical stability at the operating temperature. The characteristics of the aerosol depend on the nature of the liquid, as well as on the frequency and intensity of the ultrasonic device. An increase in ultrasonic frequency leads to a reduction in droplet diameter. When comparing pneumatic and ultrasonic generators, the latter typically produces droplets that are an order of magnitude smaller. The deposition process can be described in terms of several key parameters, namely: carrier gas flow rate, precursor solution concentration, solution flow rate, droplet radius, nozzle-to-substrate distance, substrate temperature, and ultrasonic transducer frequency [5]. A schematic representation of this device is shown in Figure 1. Appropriate control of these parameters allows the production of thin films with properties tailored to the specific objectives of the intended application.

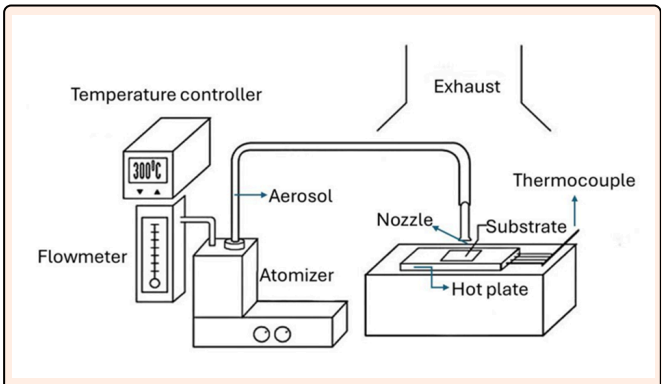

Figure 1: Schematic diagram for the ultrasonic spray pyrolysis technique.

Photoluminescent Materials

The research group led by Martínez Martínez et al. begins by proposing materials endowed with photoluminescent properties. But what is photoluminescence? Photoluminescence refers to the emission of visible light as a result of exciting a luminophore with ultraviolet radiation. It is important to emphasize that such photoluminescent materials may also be exploited as electroluminescent media, particularly for LED applications. In this context, the following section outlines some of the most recent investigations carried out using the ultrasonic spray pyrolysis (USP) technique. The research efforts of Martínez Martínez et al. have resulted in the development of photoluminescent materials spanning the synthesis and characterization of thin films and nanostructured powders. These materials exhibit emission across different regions of the visible spectrum, namely blue, green, and red. To this end, rare-earth-based phosphors are employed, owing to their well-established ability to deliver high-intensity light emission. By means of the USP technique, the group has been able to report and disseminate a series of significant contributions in this field.

Polycrystalline HfO_2 and Al^{3+}-doped HfO_2 coatings were synthesized using the USP technique. Their photoluminescence and cathodoluminescence responses were systematically investigated as a function of key synthesis parameters, namely the deposition temperature and Al^{3+} dopant concentration. Depending on substrate temperature, dopant level and excitation wavelength, the coatings exhibited blue, bluish-white and warm-white emissions. An increase in deposition temperature led to a marked enhancement of photoluminescence intensity, whereas higher dopant concentrations induced a quenching effect. The corresponding CIE chromaticity coordinates (0.3067, 0.3462), (0.3091, 0.3502) and (0.3073, 0.3498) are close to those of ideal white light. Moreover, the correlated colour temperature values obtained for selected coatings indicate their potential applicability in white lighting systems [6].

Aluminium oxide thin films doped with Tb^{3+}, Ce^{3+} and Eu^{3+} were deposited by USP technique using metal-organic acetylacetonate precursors. Their photoluminescence properties were investigated for both single layers and engineered double-layer stacks. Eu- and Tb-doped films exhibit the characteristic sharp emissions arising from intra-4f radiative transitions of the trivalent rare-earth ions, whereas Ce-doped films show two broad emission bands centered at approximately 400 and 510 nm, associated with allowed 5d→4f transitions. All films display excellent surface quality, with average roughness below 3 nm and thicknesses ranging from 50 to 260 nm, while remaining highly transparent with an optical bandgap of about 5.63 eV. The double-layer architectures consisted of an initial Eu-doped layer followed by a Ce/Tb co-doped layer with variable thickness. Under 300 nm excitation, these multilayer structures exhibit a superposition of the individual dopant emissions, yielding an overall white light output. Notably, the incorporation of Ce^{3+} using organic precursors via ultrasonic spray pyrolysis has not been previously reported. This multilayer strategy enables the simultaneous integration of Eu^{3+}, Ce^{3+} and Tb^{3+} within a single, planar and morphologically homogeneous system, characteristic of films derived from metal- organic precursors. The combination of optical transparency, low roughness and efficient luminescence makes these aluminium oxide films promising candidates for future electroluminescent applications [7].

Aluminium and hafnium oxide thin films co-doped with $CeCl_3$, $TbCl_3$ and $MnCl_2$ were deposited at 300°C using USP technique. X-ray diffraction analysis reveals a broad diffuse halo characteristic of amorphous structures. Under ultraviolet excitation at 280 nm corresponding to the peak emission of AlGaN-based LEDs efficient non-radiative energy transfer from Ce^{3+} to Tb^{3+} and Mn^{2+} is observed. This process leads to the concurrent emission of donor and acceptor ions across the blue, green, yellow and red spectral regions, yielding cold white light. The resulting chromaticity coordinates and correlated colour temperatures are (0.30, 0.32) with 7300 K for the A_2O_3: Ce^{3+}: Tb^{3+}: Mn^{3+} film, and (0.32, 0.37) with 6400 K for the HfO_2: Ce^{3+}: Tb^{3+}: Mn^{3+} film. These results indicate that such oxide thin films are promising candidates for phosphor layers in AlGaN-based LED systems aimed at efficient cold white light generation [8].

Zinc aluminate ($ZnAl_2O_4$) thin films, undoped as well as singly doped and co-doped with trivalent terbium (Tb^{3+}) and europium (Eu^{3+}) ions, were deposited by USP technique. The photoluminescent and cathodoluminescent properties were systematically investigated as a function of dopant concentration and excitation wavelength. X-ray diffraction confirmed that films deposited at 550°C crystallise in the cubic spinel structure characteristic of gahnite, irrespective of dopant incorporation. The average crystallite size, estimated using the Scherrer equation, was approximately 38 nm.

Scanning electron microscopy revealed rough surfaces composed of clusters of spherical particles with diameters in the 2-4 µm range, while energy-dispersive spectroscopy indicated a chemical composition close to the stoichiometric $ZnAl_2O_4$ and a homogeneous spatial distribution of the constituent ions. Undoped $ZnAl_2O_4$ films exhibited a broad emission spanning most of the visible region, dominated by a violet- blue band centred at ~410 nm, attributed to the host lattice. Films singly doped with Tb^{3+} or Eu^{3+} displayed the characteristic green and red emissions of these ions, respectively. In co- doped $ZnAl_2O_4$:(Tb^{3+}, Eu^{3+}) films, the superposition of host-related emission and the optical transitions of Tb^{3+} and Eu^{3+} enabled fine tuning of the emitted colour across blue, green, red, yellow, orange and, notably, white. The emission chromaticity was controlled by adjusting the Eu^{3+}/Tb^{3+} ratio and the excitation wavelength, with the optimum sample yielding CIE chromaticity coordinates of (0.3364, 0.3305), very close to ideal white light. Under electron-beam excitation, the films also exhibited multicolour CL emission, with the exception of the violet–blue host contribution and pure white emission. Overall, this study demonstrates a versatile and effective strategy for achieving tunable multicolour and white-light emission from $ZnAl_2O_4$ based thin films through controlled rare-earth doping and excitation conditions. These materials show clear potential for applications in solid-state lighting, photonics and full-colour display technologies [9].

The photoluminescence behaviour of aluminium oxide thin films doped with $CeCl_3$, $DyCl_3$ and $MnCl_2$ and deposited by USP technique was systematically investigated by excitation, emission and decay-time spectroscopy. Upon UV excitation at 278 nm corresponding to the peak emission wavelength of AlGaN-based LEDs a non-radiative energy transfer from Ce^{3+} to Dy^{3+} and Mn^{2+} was clearly identified. This process promotes the simultaneous emission of the activator ions across the blue, green, yellow and red spectral regions, yielding white light emission with CIE 1931 chromaticity coordinates of x = 0.34 and y = 0.23, characteristic of cold white light with a correlated colour temperature of approximately 4900 K. Thin films with nominal compositions of $98Al_2O_3$-$2CeCl_3$ and 90 Al_2O_3-$2CeCl_2$-$3DyCl_3$-$5MnCl_2$ were successfully prepared using the same deposition technique. Lifetime measurements confirm that the energy transfer from Ce^{3+} to Dy^{3+} and Mn^{2+} is predominantly non-radiative. The effective sensitization of Dy^{3+} and Mn^{2+} by Ce^{3+} enables broadband visible emission and stable cold white light generation. These results indicate that such doped aluminium oxide thin films are promising candidates for phosphor layers pumped by AlGaN-based LEDs, contributing to the development of efficient cold white light sources for solid-state lighting applications [10].

Hafnium oxide thin films singly doped with Ce^{3+}, co-doped with Ce^{3+}/Tb^{3+}, and triply doped with $Ce^{3+}/Tb^{3}/Mn^{2+}$ were synthesized

by USP technique. Structural analysis by X-ray diffraction revealed a broad diffraction halo with no discernible Bragg reflections, indicating that all films are predominantly amorphous. In the co-doped system, efficient energy transfer from Ce^{3+} to Tb^{3+} ions occur within Ce^{3+}-Tb^{3+} clusters, with an electric dipole-quadrupole interaction identified as the most plausible transfer mechanism. For the triply doped films, both Tb^{3+} and Mn^{2+} ions are effectively sensitized by Ce^{3+}, enabling their simultaneous emission under UV excitation (270 nm) and leading to cold white light with correlated colour temperatures in the range of 6400–7200 K. The energy transfer efficiency from Ce^{3+} to Tb^{3+} and Mn^{2+} increases with Mn^{2+} concentration, attaining values of up to ~76% for films containing 1.6 at.% manganese. The combination of high energy transfer efficiency and cold white light emission highlights Ce^{3+}/Tb^{3}/Mn^{2+} doped HfO_2 thin films as a versatile and promising phosphor material for UV-pumped LED architectures aimed at cold white light generation [11].

Conclusion

Collectively, these studies demonstrate that ultrasonic spray pyrolysis (USP technique) is a powerful and flexible deposition technique for the design of advanced luminescent oxide thin films. By enabling precise control over composition, dopant distribution and film architecture, USP facilitates efficient energy transfer processes and broadband visible emission, culminating in high-quality white light generation. The consistent attainment of chromaticity coordinates near the ideal white point, combined with tunable correlated colour temperatures and compatibility with UV-pumped LED platforms, underscores the technological relevance of these materials. Consequently, USP-derived doped oxide thin films emerge as highly promising candidates for next-generation phosphor layers in solid- state lighting, offering a scalable pathway towards efficient, stable and spectrally engineered white light sources.

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