FABRICATION AND CHARACTERIZATION OF $TiO_2/Cu/TiO_2$ MULTILAYER THIN FILMS FOR THERMOLUMINESCENCE DOSIMETRY USING RF/DC SPUTTERING

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LIST OF SYMBOLS

°C	Degree Celsius
α	Absorption coefficient
a_i	Fractional contents of electrons of an element
B	Kinetics order
B*	Mean thermoluminescence background signal
C	Coulomb
D	Absorbed dose
Do	Minimum detectable dose
e^-	Electron
E_g	Band gap energy
$E\alpha$	Trap depth (activation energy)
F(D)	Linearity index
h	Hour
h^+	Hole
hv	Energy of a photon
Im	Maximum intensity
k	Boltzmann's constant
K	Kelvin
λ	Wavelength
min	Minute

LIST OF ABBREVIATIONS

2D	Two-dimensional
AFM	Atomic force microscopy
BeO	Beryllium oxide
CaF_2	Calcium fluoride
CF	Calibration factor
Co	Cobalt
Cu	Copper
DC	Direct current
EDX	Energy Dispersive X-ray
FE-SEM	Field Emission Scanning Electron Microscopy
Gy	Gray
IR	Ionizing radiation
LiF	Lithium fluoride
NA	Avogadro’s number
PL	Photoluminescence
RF	Radio frequency
Ti	Titanium
TiO_2	Titanium dioxide
UV-Vis	Ultraviolet-visible light
XRD	X-ray diffraction

2D	Two-dimensional
AFM	Atomic force microscopy
BeO	Beryllium oxide
CaF_2	Calcium fluoride
CF	Calibration factor
Co	Cobalt
Cu	Copper
DC	Direct current

LIST OF APPENDICES

FABRIKASI DAN PENCIRIAN FILEM NIPIS BERBILANG LAPISAN $TiO_2/Cu/TiO_2$ UNTUK DOSIMETRI TERMOPENDARCAHAYA MENGGUNAKAN PENYEMBURAN RF/DC

ABSTRAK

Dosimetri Termopendarcahaya (TLD) merupakan peranti yang digunakan secara meluas dan diperbuat daripada bahan fosfor, seramik, dan kristal, yang dikenali kerana pengeluaran luminesens yang tinggi bagi setiap dos sinaran yang diserap. Walau bagaimanapun, ia menghadapi beberapa cabaran utama, termasuk kehilangan isyarat yang cepat, penyerakan sinaran, ketepuan pada dos tinggi, serta proses anil yang kompleks untuk penggunaan semula. Kajian ini bertujuan untuk membangunkan dosimeter filem nipis berstruktur berbilang lapisan $TiO_2/Cu/TiO_2$ yang baharu bagi mengatasi kekangan ini serta meningkatkan prestasi dan kebolehpercayaan dalam pengukuran sinaran. Dalam kajian ini, dosimeter berbilang lapisan telah difabrikasi menggunakan kaedah penyemburan frekuensi radio (RF) dan arus terus (DC), yang membolehkan kadar pemendapan lebih pantas serta menjamin ketulenan dan ketebalan lapisan yang seragam. Tiga kumpulan filem berbilang lapisan telah dihasilkan untuk analisis. Kumpulan pertama terdiri daripada satu lapisan tunggal TiO_2 tulen dengan ketebalan 20, 30, 50, 100, dan 150 nm. Kumpulan kedua berstruktur TiO_2 (150 nm)/Cu (25 nm)/TiO_2 (x nm), dengan nilai x sebanyak 20, 30, 50, 100, dan 150 nm. Kumpulan ketiga terdiri daripada struktur TiO_2 (150 nm)/Cu (x nm)/TiO_2 (50 nm), dengan nilai x sebanyak 5, 10, 25, 40, dan 50 nm. Ciri struktur, morfologi dan optik filem telah dianalisis menggunakan pelbagai teknik, termasuk XRD, UV-VIS, FESEM, EDX, AFM, dan PL. Filem berbilang lapisan ini menunjukkan tindak balas yang baik terhadap pendedahan sinaran-X dan gamma sehingga 1500 mGy. Pengukuran

sensitiviti menunjukkan bahawa filem ini kira-kira 2.25 kali kurang sensitif berbanding TLD-100 bagi sinaran X dan kira-kira 9.8 kali kurang sensitif bagi sinaran gamma. Keamatan termoluminasi (TL) optimum dikenal pasti dalam konfigurasi TiO_2 (445 nm)/Cu (14.2 nm)/TiO_2 (130 nm), dengan keamatan TL tertinggi dicapai selepas rawatan anil pada suhu 400°C selama 2 jam. Dos boleh dikesan minimum (MDD) adalah 4.549 mGy, dan kadar pemanasan optimum untuk lengkung cahaya TL ialah 5°C/saat. Dapatan kajian ini menunjukkan bahawa filem berbilang lapisan TiO_2/Cu/TiO_2 berpotensi besar dalam aplikasi dosimetri termopendarcahaya.

FABRICATION AND CHARACTERIZATION OF TiO_2/Cu/TiO_2 MULTILAYER THIN FILMS FOR THERMOLUMINESCENCE DOSIMETRY USING RF/DC SPUTTERING

ABSTRACT

Thermoluminescent dosimeters (TLDs) are widely used devices made from phosphors, ceramics, and crystals, known for their high luminescence output per absorbed dose. However, they face significant challenges, including rapid signal fading, radiation scattering, saturation at high doses, and complex annealing processes for reuse. This study aims to develop a novel TiO_2/Cu/TiO_2 multilayer thin film dosimeter that addresses these limitations, improving the performance and reliability of radiation measurement. The multilayer dosimeters were fabricated using radio-frequency (RF) and direct current (DC) sputtering methods, enabling faster deposition rates while ensuring high purity and uniformity. Three batches of multilayer films were produced for analysis. The first batch included a single layer of pure TiO_2 with thicknesses of 20, 30, 50, 100, and 150 nm. The second batch was structured as TiO_2 (150 nm)/Cu (25 nm)/TiO_2 (x nm), with x values of 20, 30, 50, 100, and 150 nm. The third batch consisted of TiO_2 (150 nm)/Cu (x nm)/TiO_2 (50 nm), with x values of 5, 10, 25, 40, and 50 nm. We analyzed the structural, morphological, and optical properties of the films using various techniques, including XRD, UV-VIS, FESEM, EDX, AFM, spectroscopy, and PL spectroscopy. The multilayer films demonstrated favorable responses to X-ray and gamma-ray exposure, tested up to 1500 mGy. The sensitivity measurements revealed that the films were approximately 2.25 times less sensitive than TLD-100 for X-rays and about 9.8 times less sensitive for gamma rays. The optimal TL intensity was identified in the TiO_2 (445 nm)/14.2 nm Cu/TiO_2 (130

nm) configuration, with the highest TL intensity achieved after an annealing treatment at 400°C for 2 hours. The minimum detectable dose (MDD) was found to be 4.549 mGy, and the optimal heating rate for the TL glow curve was determined to be 5°C/sec. The findings indicate that TiO_2/Cu/TiO_2 multilayer films are promising candidates for TL dosimetric applications.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Thermoluminescent dosimeters (TLDs) have been proven to be highly effective tools for detecting ionizing radiation doses. They offer numerous advantages, including ease of handling, simple TLD readout procedures, and the utilization of TL glow curves for quality control and dose estimation. Furthermore, TLDs enable individual calibration and exhibit very flat responses to photon energies, which makes them particularly suitable for precise measurements (McKeever and Moscovitch, 2003). In addition, TLDs can integrate dose accumulation over time and demonstrate considerable sensitivity to different forms of radiation, even at minimal sizes, rendering them more effective than many other dosimeters for measuring absorbed doses of ionizing radiation.

TLD materials possess appealing intrinsic properties such as a favorable effective atomic number (Z_{eff}), reasonable sensitivity, an energy-independent dose response, a wide linear dynamic range, rapid preparation, low manufacturing costs, and low fading rates (Kaur et al., 2020). Because of their compact dimensions, thermoluminescent detectors are especially appropriate for mapping radiation fields in medical applications of ionizing radiation, as well as for environmental monitoring and personal dosimetry (Aluker et al., 2016). Nonetheless, achieving high accuracy and precision in radiation dose measurement remains a significant challenge in many dosimetric applications.

A variety of materials have been utilized as TLD phosphors, including LiF, $Li_2B_4O_7$, MgB_4O_7, and BeO, which are often referred to as tissue-equivalent materials because their effective atomic numbers are close to that of human soft tissue (Z_{eff} = 7.4) (Jayachandran, 1971). In contrast, phosphors with atomic numbers ranging from 15 to 18, such as salts of alkaline earth metals and metal oxides including $CaSO_4$, CaF_2, Al_2O_3, ZrO_2, and TiO_2, exhibit higher sensitivity, although they do not possess tissue equivalence (Azorín-Nieto, 1990).

Recent research has increasingly focused on the development of nanomaterials that maintain physical and chemical stability under both low and high doses of radiation. For instance, rod-shaped nanophosphor materials have demonstrated linear TL responses across a broad dose range (0.1 Gy to 10 kGy) with low fading. LiF: Cu, P, Mg TLDs have shown TL sensitivities approximately three times higher than bulk LiF: Mg, Ti (TLD-100) phosphors (Salah, Sahara et al., 2007). Similarly, the TL sensitivity of MgB_4O_7:Dy nanophosphor was reported to be 0.025 times greater than that of bulk $CaSO_4$:Dy (Lochab et al., 2007). $Li_2B_4O_7$:Cu nanophosphors have demonstrated superior linear response and sensitivity compared to commercially available microcrystalline forms (Singh et al., 2011).

Current research efforts are emphasizing the synthesis of TLD materials incorporating nanostructured components, especially in the form of thin films. Such materials exhibit unique properties that differ markedly from their bulk counterparts due to their large surface area-to-volume ratios. The incorporation of nano-TLD components not only enhances the sensitivity and stability of thermoluminescent materials but also facilitates the miniaturization of electronic components and improves their performance in measuring low-energy radiation doses (Azorín, 2014).

This study focuses on evaluating the radiation dosimetric response of a three-layer TiO_2/Cu/TiO_2 thin film structure under controlled X-ray irradiation. The choice of this specific multilayer configuration, instead of a single TiO_2 layer, is based on its potential to enhance charge transport, improve sensitivity, and achieve superior mechanical stability. The investigation is limited to copper as the intermediate conductive layer and does not extend to other metals or semiconductor combinations.

1.2 Problem statement

Although TLD-100 (LiF: Mg, Ti) remains one of the most widely used materials in radiation dosimetry, its long-term applicability is hindered by several drawbacks, including susceptibility to environmental moisture, the requirement for complex annealing cycles, rapid signal fading, dose saturation at high exposures, and limited thermal stability (McKeever, 1995a; Salah & Sahara, 2007; Swamy et al., 2014). Furthermore, while its effective atomic number ($Z_{eff} \approx 8.2$) provides near tissue-equivalence and makes it suitable for medical applications, the material's complex glow curve structure often complicates precise dose evaluation under varying irradiation conditions.

Alternative dosimeters such as CaF_2:Dy (TLD-200) and LiF: Mg, Cu, P (TLD-100H) have been developed to improve sensitivity; however, they continue to suffer from severe signal fading and instability at elevated temperatures (Binder et al., 1969; Nair et al., 2018). These limitations highlight the need for novel dosimetric materials that combine high sensitivity with superior thermal and environmental stability.

Recent developments in thin-film technology have introduced titanium dioxide (TiO_2) as a promising candidate for thermoluminescence (TL) applications due to its excellent chemical stability, wide bandgap, high radiation resistance, and ability to form nanostructures with tunable optical properties (Maurício et al., 1999; Thabit et al., 2021, 2023). Unlike bulk TLD-100, thin-film systems offer the advantages of miniaturization, easy integration with microelectronic devices, and tunable dosimetric response through controlled thickness and multilayer architectures.

Incorporating metallic interlayers such as copper (Cu) within TiO_2 multilayers provides an additional pathway to enhance TL performance. Copper can introduce efficient charge-trapping and recombination centers, improve carrier transport, and potentially increase sensitivity by facilitating energy transfer between layers. These properties may allow TiO_2/Cu/TiO_2 multilayer thin films to overcome the drawbacks of TLD-100 by providing higher sensitivity, improved thermal stability, and reduced signal fading under ionizing radiation. Despite this potential, systematic studies on TiO_2/Cu/TiO_2 multilayer thin films are scarce, and the influence of deposition parameters, interlayer effects, and film thickness on TL response remains largely unexplored (El Hajj et al., 2012).

To address these gaps, this study proposes the fabrication and characterization of TiO_2/Cu/TiO_2 multilayer thin films using magnetron sputtering. By comparing their thermoluminescent properties against the benchmark TLD-100 and investigating how structural design, deposition conditions, and interlayer engineering affect performance under ionizing radiation, this research seeks to advance the development of a new class of miniaturized, high-sensitivity, and thermally stable dosimeters for medical, industrial, and environmental radiation monitoring.

1.3 The motivation behind the research

Radiation dosimetry plays a vital role in healthcare, environmental safety, industrial quality assurance, and radiation protection. Its success is intrinsically tied to the properties of the dosimetric materials used. For example, in low-energy applications such as mammography, a dosimeter must exhibit suitable energy dependence and stable signal retention. Efficient TL materials must facilitate high electron-hole pair generation, strong trapping mechanisms, and stable luminescent emission (Tang et al., 2021). Crystalline TL materials are common due to their light scattering properties, which enhance signal detection (Saidu et al., 2018). However, many suffer from opacity, thermal instability, or limited reproducibility.

This research is motivated by the need for a robust, energy-independent TL material that provides clear glow curves, wide linear response ranges, high sensitivity, and minimal fading. Titanium dioxide (TiO_2) stands out as a potential candidate due to its wide bandgap (3.2 eV), excellent optical and chemical stability, mechanical strength, and strong adhesion to glass (Dhar & Alford, 2014). However, its relatively high Z_{eff} results in pronounced energy dependence. Incorporating copper (a low-Z metal) as an interlayer may correct for this, helping to minimize backscatter effects and redundant radiation, thereby flattening the energy response (Pradhan et al., 1990)

1.4 Research objectives

This study primarily aims to develop and evaluate TiO_2/Cu/TiO_2 multilayer thin film thermoluminescent dosimeters with enhanced sensitivity, stability, and dosimetric performance for radiation monitoring. The specific objectives are as follows:

i. To fabricate TiO_2/Cu/TiO_2 multilayer thin films using direct current (DC) and radiofrequency (RF) sputtering techniques, with top TiO_2 layer thicknesses varied systematically between 20 nm and 150 nm.

ii. To characterize the structural, morphological, and optical properties of the fabricated thin films using XRD, FE-SEM, EDX, AFM, and UV–Vis spectroscopy.

iii. To evaluate the thermoluminescent and dosimetric properties of the multilayer films, including glow curve profile, dose–response linearity in the range of 100–1500 mGy, reproducibility, sensitivity, minimum detectable dose (MDD), thermal fading, and kinetic trapping parameters.

iv. To compare the performance of the fabricated dosimeters with that of the commercial TLD-100 material, particularly in terms of sensitivity, and under X-ray irradiation.

1.5 Significance of the study

This study contributes to the advancement of thin-film thermoluminescent materials by introducing a novel TiO_2/Cu/TiO_2 multilayer system. Its findings have potential implications for the design of low-cost, miniaturized dosimeters with enhanced sensitivity, suitable for medical imaging, radiotherapy, and environmental radiation monitoring (Kher & Bhatt, 2021; Abdelhalim et al., 2020). Moreover, the research fills a critical gap in the understanding of nanostructured TL materials and their interaction with ionizing radiation (Yukihara & McKeever, 2011; Rivera et al., 2015).

1.6 Scope of the study

This study focuses on the development and comprehensive evaluation of TiO_2/Cu/TiO_2 multilayer thin films deposited on glass substrates, fabricated via magnetron sputtering techniques. The research involves the optimization of key deposition parameters, including the thicknesses of the individual layers and the applied plasma power, to enhance thermoluminescent performance. Structural and morphological characterization of the films is conducted using X-ray diffraction

(XRD) and field emission scanning electron microscopy (FE-SEM), while elemental composition is analyzed through energy dispersive X-ray spectroscopy (EDX). Optical properties, including absorption and transmittance, are examined using ultraviolet-visible (UV–Vis) spectroscopy, and photoluminescence (PL) spectroscopy is utilized to investigate emission characteristics.

The dosimetric evaluation encompasses exposure of the films to both X-ray and gamma radiation, followed by thermoluminescent (TL) readout using a standard TLD reader. The assessment includes analysis of dose–response behavior within a defined dose range, measurement reproducibility, investigation of thermal and optical fading, determination of the minimum detectable dose (MDD), and kinetic trap analysis through glow curve deconvolution techniques. The optimized multilayer samples identified based on the most effective configuration of TiO_2 top and bottom layer thicknesses and the intermediate Cu layer are further compared with the commercially available TLD-100 dosimeter. This comparison specifically focuses on thermoluminescent sensitivity and dose–response characteristics. Other performance aspects, such as long-term stability, energy dependence, or performance under clinical and environmental radiation conditions, are beyond the scope of this work. The overall aim is to assess the potential of TiO_2/Cu/TiO_2 multilayer thin films as a promising alternative dosimetric material relative to conventional TLD-100.

1.7 Thesis outline

This thesis is organized into five chapters to systematically present the research process and findings. Chapter 1 introduces the study by outlining the background, problem statement, research motivation, objectives, scope, research gap, and the structure of the thesis, providing a comprehensive framework for the investigation.

Chapter 2 presents a review of the fundamental principles of thermoluminescence, key dosimetric materials, and previous studies related to TiO_2 thin films in radiation dosimetry. It also covers relevant theoretical models and summarizes significant experimental findings from the literature. Chapter 3 describes the experimental methodology, including materials selection, deposition of multilayer thin films using radio frequency (RF) and direct current (DC) sputtering techniques, and the characterization methods employed. These include X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), ultraviolet-visible (UV–Vis) spectroscopy, photoluminescence (PL) spectroscopy, and thermoluminescence dosimetry (TLD) protocols.

Chapter 4 presents and analyzes the results obtained from structural, morphological, optical, and dosimetric evaluations, with emphasis on glow curve analysis and kinetic modeling. Finally, Chapter 5 summarizes the major findings of the study, assesses the extent to which the research objectives were fulfilled, discusses limitations encountered during the investigation, and proposes recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the theoretical and experimental background relevant to this research. It begins with the principles of thermoluminescence (TL), including energy storage and release, radiation sources, and interactions of ionizing radiation with matter, followed by the characteristics and applications of conventional TLDs in medical and industrial dose assessment. Thin-film dosimetry is introduced as an alternative to bulk materials, offering advantages such as higher spatial resolution and surface conformity.

The focus then shifts to titanium dioxide (TiO_2) as a promising dosimetric material due to its optical and luminescent properties. Prior work on thin-film TL systems, including doped and multilayer structures, is reviewed to show how fabrication methods and structural design influence performance. Particular attention is given to TiO_2/Cu/TiO_2 multilayers, where the Cu interlayer modifies trap distributions and charge recombination, providing a structural route beyond chemical doping. This context establishes the rationale for exploring multilayer TiO_2/Cu/TiO_2 thin films in the present study.

2.2 Luminescence phenomena

Luminescence refers to the light emission resulting from electronic excitation in materials, with specific excitation mechanisms offering direct relevance to thin-film dosimetry. Photoluminescence, for instance, is widely used to probe defect states in TiO_2, where peaks near 400–500 nm are associated with oxygen vacancies (Zhou et al., 2019). In contrast, radioluminescence helps assess radiation response in multilayer oxides through emission intensity correlated with trap density (Rahman et al., 2020). The distinction between fluorescence ($\tau \leq 10^{-8}$ s) and phosphorescence ($\tau \geq 10^{-8}$ s) is crucial, as TiO_2 systems often exhibit both fast band-edge emission and slower defect-mediated afterglow, which is exploited in TLDs (Chen & McKeever, 1997; Lakshminarayana et al., 2017).

Thermoluminescence provides a time-integrated record of radiation dose, as demonstrated in oxide nanomaterials and multilayer thin films (Wang et al., 2018). These luminescence processes form the theoretical basis for understanding defect-related emission and glow curve behavior in TiO_2/Cu/TiO_2 multilayer dosimetric systems. Table. 2.1 presents a list of luminescence phenomena and the techniques utilized to stimulate them.

Table 2.1 The phenomenon of luminescence and the methods of stimulation (Valeur & Berberan-Santos, 2012).

Luminescence phenomenon	Method of excitation
Bioluminescence	Biochemical reactions
Cathodoluminescence	Electron beam
Chemiluminescence	Chemical reactions
Electroluminescence	Electric field
Photoluminescence	UV and infrared light
Piezoluminescence	Pressure (10 tons m^{-2})
Triboluminescence	Friction
Radioluminescence	Ionizing radiation
Sonoluminescence	Sound waves
Fluorescence Phosphorescence Lyoluminescence Thermoluminescence	Ionizing radiation, UV, and visible light

2.2.1 The luminescence centers in the (TL) light emission

Luminescent centers are structural defects or dopant atoms embedded in the host lattice that act as discrete sites for capturing and releasing charge carriers. Instead of considering them only in general terms, research in oxide-based thin films shows that such centers strongly influence the shape and intensity of TL glow curves. For example, oxygen vacancies in TiO_2 create deep-level traps within the band gap, which contribute to characteristic TL peaks under ionizing radiation (Bharti et al., 2016). Similar findings were reported by Morozova et al. (2001), who observed that dopants such as Cu^{2+} enhance carrier trapping efficiency, thereby increasing light yield. These studies confirm the theoretical role of luminescent centers as recombination sites (Furetta, 2003b), but they also demonstrate their practical importance in tailoring TL sensitivity in thin film dosimetric systems.

2.2.2 TL: Historical perspective and research Use

The phenomenon of TL has been recognized since Boyle's early observations of glowing diamonds, but its scientific relevance to dosimetry became apparent in the mid-20th century, when the need for reliable radiation monitoring grew. McKeever (1985) defined TL as the thermally stimulated emission of light following prior radiation absorption, a description still foundational today. Since the 1940s, TL has been systematically applied in dosimetry, and extensive studies have demonstrated its reliability for recording accumulated radiation doses (Duragkar et al., 2019). Beyond radiation protection, TL has also been utilized as a chronological tool in archaeology and geology (Chen & McKeever, 1997). In recent decades, the focus has shifted toward nanostructured and thin-film TL materials, where reduced dimensionality allows for enhanced trapping and controlled luminescence properties (Rathore et al., 2023). This evolution illustrates how the historical foundation of TL has developed into a modern research tool for advanced applications.

2.2.3 TL dosimetry materials

The effectiveness of TL materials depends on their ability to store energy in metastable traps and release it as light during heating. Classical studies established that insulating or semiconducting hosts such as LiF, CaF_2, and Al_2O_3 could be tailored through dopants to enhance trap depth and stability (Bos, 2006). Daniels et al. pioneered TL as a dosimetric technique, and subsequent development of LiF: Mg, Ti (TLD-100) by Harshaw Chemical Company set the standard for commercial TL detectors (Bhatt & Kulkarni, 2014). Current research has expanded to a wide variety of hosts, such as $Li_2B_4O_7$: Mn, Al_2O_3:C, and BeO, each optimized for specific applications (Bos, 2017). More recently, investigations have extended into nanostructured and thin-film oxide systems, where defect engineering enables enhanced sensitivity at reduced material quantities (Ding et al., 2020).

Understanding TL mechanisms in these materials requires advanced experimental techniques such as glow curve deconvolution, photoluminescence, and electron paramagnetic resonance to map trap distributions and recombination dynamics. Such studies not only explain the dosimetric performance of conventional phosphors but also provide insight into novel multilayer thin films, including TiO_2/Cu/TiO_2 systems, where engineered interfaces play a critical role in trap-assisted luminescence(Bhatt and Kulkarni, 2014). Table 2.2 presents some characteristic dosimetric properties of the frequently utilized TL materials for radiation dosimetry.

Table 2.2 Lists of general characteristics of commercial TL materials dosimeters (Bhatt and Kulkarni, 2014).

TLD type	Z_{eff}	Main peak (°C)	Relative Sensitivity	Fading (dark room)	Useful dose range
LiF: Mg,Ti	8.14	200	1	5% per year	$20\mu - 10Gy$
$LiF: Mg, Cu, P$	8.14	210	40	5% per year	$0.2\mu - 10Gy$
$Li_2B_4O_7: Mn$	7.30	220	0.40	4% per month	$0.1mG - 3Gy$
$Li_2B_4O_7: Cu$	7.30	205	8	10% per 2 months	$10\mu - 10^3Gy$
$MgB_4O_7: Dy$ or Tm	8.40	190	$6 - 7$	4% per month	$5\mu Gy - 50Gy$
BeO	7.10	190	~ 1.00	8% per 2 months	$0.1 - 0.5Gy$
$CaSO_4: Dy$	15.30	220	30	1% per 2 months	$2\mu Gy - 10Gy$
$CaF_2: Dy$	16.30	215	15	8% per 2 months	$10\mu - 10Gy$
$Al_2O_3: C$	10.20	190	60	5% per year	$0.1\mu - 10Gy$

2.2.4 Mechanism of TL

The mechanism of thermoluminescence is widely understood within the framework of solid-state physics, but its detailed investigation provides important insights into the dosimetric performance of different materials. TL arises from the trapping of charge carriers in metastable defect levels within the band gap of insulators and semiconductors, followed by their release during thermal stimulation. Recent studies have shown that the distribution, depth, and stability of these traps largely dictate the glow curve structure and sensitivity of TL materials (Chen & McKeever). In thin-film dosimetric systems, particularly TiO_2-based multilayers, trap populations can be significantly altered by structural defects, dopant incorporation, and interfacial effects, making the mechanism central to understanding their radiation response (Wang et al., 2020). As illustrated in Figure 2.1, both the electron and h^+ traps are unoccupied before irradiation, allowing for a state of equilibrium between electrons and holes (Rivera, 2012).

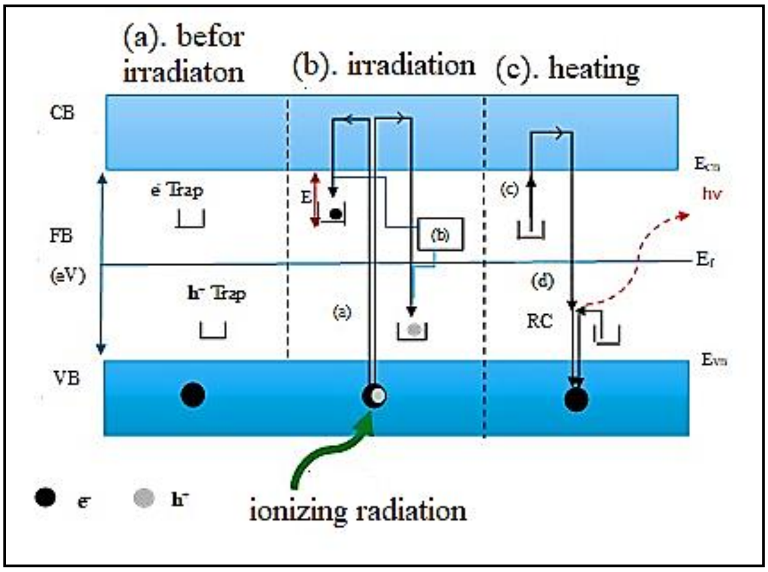

Figure 2.1 The thermoluminescence phenomenon process, where transitions **a**, **b**, **c**, and **d** represent the different electron transitions (McKeever, 1995a).

2.2.4(a) Before irradiation

Before irradiation, electrons predominantly occupy the valence band, leaving defect-related traps in the band gap unfilled. These traps, which may arise from oxygen vacancies, substitutional dopants, or lattice distortions, act as potential capture sites for charge carriers (Rivera, 2012). In TiO_2, for instance, oxygen vacancies introduce electron traps just below the conduction band, while cation-related defects can produce hole traps near the valence band (Gurylev, 2021). The presence and concentration of these traps strongly influence subsequent TL processes, as they determine the number of carriers that can be stored upon irradiation.

2.2.4(b) Irradiation

When a thermoluminescent material is exposed to ionizing radiation with energy above its band gap, electrons are promoted from the valence band to the conduction band, leaving behind holes in the valence band. These free carriers are subsequently captured by defect-related traps within the band gap. The efficiency of this process depends strongly on the type and distribution of traps present. In oxide-based materials, oxygen vacancies often act as electron traps near the conduction band, while cation defects can function as hole traps near the valence band (Rivera, 2012; Gurylev, 2021). Experimental studies have confirmed that radiation exposure increases the population of trapped carriers, which directly correlates with the intensity of thermoluminescence upon heating (Bos, 2006). In TiO_2/Cu/TiO_2 multilayer systems, the irradiation stage is particularly important because the presence of interfacial states and Cu-related defects enhances trapping efficiency, thereby modifying the dose–response behavior.

2.2.4(c) Heating

Upon heating, trapped carriers acquire sufficient thermal energy to escape from their metastable states into the conduction or valence bands. These free carriers migrate until they recombine at luminescent centers, releasing energy in the form of photons (McKeever, 1995a). The spectral distribution of this emission depends on the depth of the trap and the nature of the recombination center, with shallow traps producing low-temperature glow peaks and deep traps producing high-temperature peaks. Several studies have demonstrated that glow curve deconvolution provides insight into trap depth and kinetics, thereby linking the observed TL signal to the underlying defect structure (Chen & McKeever, 1997; Furetta, 2003b).

In TiO_2 thin films, defect-mediated recombination often results in broad visible emissions attributed to oxygen vacancies, while Cu incorporation introduces additional recombination pathways that enhance photon yield. These findings highlight how the heating stage not only produces detectable luminescence but also reveals the defect landscape of the material, making it a powerful diagnostic tool for thin-film dosimetry research.

Due to the process of photon emission, which includes releasing a few traps at various energies, the charge carriers are released at different temperatures, yielding a glow curve that is characteristic of a material exhibiting one or more peaks. This mechanism is critical to elucidating radiation dosimetry as it shows that the number of released photons is proportional to the dose of absorbed radiation. However, some electrons and holes are trapped in semiconductors or insulators: electrons in $\mathbf{e}^-$ trap and holes in h^+ trap or recombination centers (RC). The heating of the material can cause electrons and holes to escape from these traps via thermal stimulation (TS). The Arrhenius Equation. 2.1 explains the probability (p) of an electron being released from a trap per unit of time.

$$p = \text{sexp}\left(-\frac{E}{kT}\right) \tag{2.1}$$

The pre-exponential factor S (s^{-1}) is referred to as the frequency factor or the attempt-to-escape factor (not temperature dependent), which is dependent on the rate at which an electron is incident on the trap. (E) denotes the trap depth or activation energy needed to release an electron into the CB. It is measured, in (eV), from the trap level to the bottom of the CB. In the case of a hole trap, (E) is measured from the trap to the top of the VB. (E) and (S) are key as trap parameters. (T) and (k) represent absolute temperature and Boltzmann`s constant (i.e., 8.617×10^{-5} eV/K), respectively (Furetta, 2003a).

S and E are important because they control the expulsion of an electron from the trap at a specific temperature. Equation. 2.2 expresses the lifetime (τ) of the charge carrier in the metastable condition (i.e., where the charge carriers are trapped) at temperature T:

$$\tau = p^{-1} \tag{2.2}$$

In addition, if T_o is the temperature at which the material is subjected to radiation, subsequently any electrons and holes will stay trapped at the e^- trap and h^+ trap or RC, respectively, for a protracted duration, even after exposure to radiation in the case of E >> T_o (K). The possibility of partition increases when the temperature of the material increases from T_o (K) to T (K). Afterward, the trapped electrons are liberated from the e-trap and drift about in the conduction band pending recombination of the electrons in the h^+ trap, or RC. Thus, RC attains the maximum state of excitation and then rebounds to the ground state by the process of light emission (hv) or thermoluminescence (TL). Recombination causes light emission, also referred to as "radiative" transitions, for luminescence.

In contrast, during a non-radiative transition, no light is emitted, and the released energy is observed only as phonon emission (lattice vibrations). In TL, at a given heating time t, the TL intensity I(t) (in photons per second) depends on the recombination rate of electrons (e^-) and holes (h^+) at recombination centers (RC). If m (m^{-3}) represents the concentration of trapped charge carriers at RC, the TL intensity can be expressed as an equation. 2.3:

$$I(t) = -\frac{dm}{dt} = -\frac{dn}{dt} = np = n_s \exp\left(-\frac{E}{kT}\right) \tag{2.3}$$

The negative sign indicates the decrease in the concentration of trapped carriers (e^-or h^+) as recombination proceeds. Equation. 2.3 therefore describes the release and transfer of charges within the crystal lattice, which gives rise to TL emission.

2.3 Radiation sources in TL dosimetry studies

(TLDs) are typically evaluated under controlled radiation fields, and the choice of source strongly influences the observed glow curve characteristics, sensitivity, and dose–response behavior. Different studies have employed gamma, beta, and X-ray sources to investigate material performance, each providing insight into specific aspects of trapping and recombination processes. Gamma-emitting isotopes such as ^{60}Co and ^{137}Cs are widely used in TL studies due to their well-characterized photon energies and dose rates. For example, Bos (2006) and Bhatt & Kulkarni (2014) reported consistent linear dose–response of conventional phosphors such as LiF: Mg,Ti, and Al_2O_3:C under gamma irradiation, establishing these sources as reference standards in dosimetry research. Gamma rays also allow examination of bulk sensitivity in thin films, where interaction probabilities differ from conventional powders.

Beta-emitting sources, particularly ^{90}Sr–^{90}Y, are employed to probe shallow dose distributions and surface sensitivity. Villarreal-Barajas et al., (2002) demonstrated that nanostructured oxide thin films exhibit strong thickness-dependent TL yield under beta irradiation, highlighting the role of defect density and trapping depth in films below 200 nm. Such findings are relevant for TiO_2 multilayers, where the top layer thickness influences both absorption and charge carrier transport.

X-ray sources have gained attention in recent years due to their direct relevance to diagnostic and therapeutic radiology. Luo et al. (2017) showed that oxide nanostructures display enhanced TL sensitivity to diagnostic X-rays, attributed to the presence of shallow traps and surface states. In our earlier work (Idriss et al., 2023), we presented a preliminary study on the effect of TiO_2 layer thickness on radiation response. More recently, we demonstrated that X-ray irradiation of TiO_2 multilayer thin films with a Cu interlayer significantly modifies the glow-curve characteristics due to the formation of interfacial traps and altered recombination kinetics. Building on these findings, the present thesis expands the investigation to TiO_2/Cu/TiO_2 multilayer systems, reinforcing the suitability of X-ray excitation for probing defect states in oxide thin-film dosimeters.

Overall, the literature demonstrates that radiation sources are not only chosen for practical convenience but also to probe specific material responses. Gamma irradiation is often used for calibration and bulk sensitivity studies, beta irradiation for surface and thin-film effects, and X-rays for investigating trap-assisted recombination in oxide films. For the present work, X-ray sources are most relevant because they provide a direct means to study the influence of multilayer architecture on TL response, particularly the role of Cu interlayers and TiO_2 thickness variation.

2.3.1 Interaction of radiation with matter in TL dosimetry

Radiation interacts with matter through several well-established mechanisms, primarily photoelectric absorption, Compton scattering, and pair production, each dominant in different photon energy ranges (Knoll, 2010). While these interactions are fundamental to radiation physics, their practical relevance to thermoluminescent dosimeters varies, and only some directly contribute to the generation of trapped charge carriers responsible for TL. As shown in Figure 2.2, photo-absorption, pair production, and Compton scattering dominate the total cross section at low photon energies, high energies, and intermediate energy ranges, respectively.

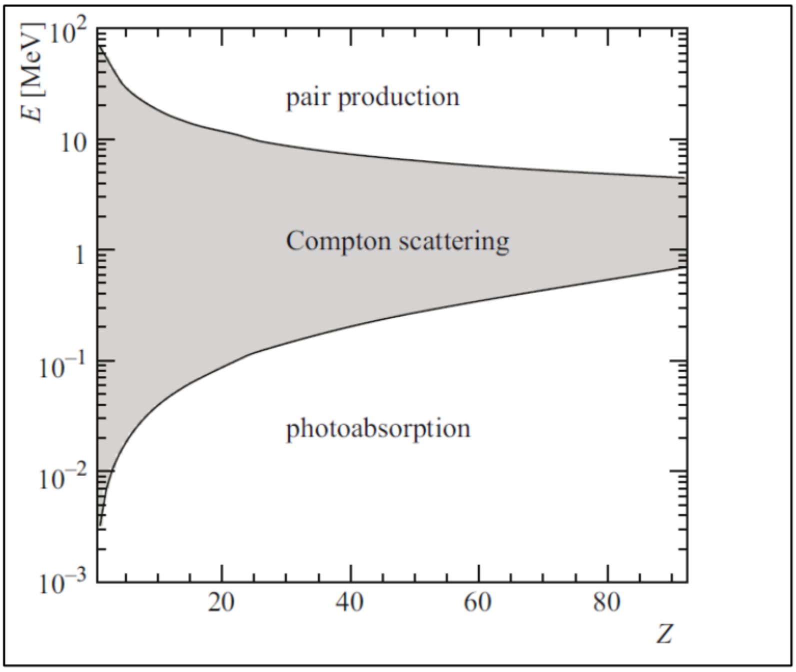

Figure 2.2 The bottom curve shows the trend of the photon energy E as a function of the target substance's atomic number Z, below which photoelectric absorption (photoabsorption) is the main response mechanism, while the upper curve shows the energy above which pair production is dominant. The shaded area between the two curves represents the Compton scattering-dominated field (Fabjan, 2020).

2.3.2 Photoelectric effect

The photoelectric effect is the most important mechanism for TL materials, particularly in low- to medium-energy photons typical of diagnostic X-rays. When a photon is absorbed by a material, it ejects an electron, creating an electron–hole pair that can be captured in defect-related traps (Bos, 2006; Khan & Gibbons, 2014). Materials with higher effective atomic numbers exhibit stronger photoelectric absorption, enhancing TL sensitivity. In TiO_2 thin films, studies have shown that oxygen vacancies and other defect centers act as effective electron traps, and variations in film thickness modify absorption probabilities and glow curve characteristics. These findings demonstrate that optimizing the density and type of defects can directly improve dosimetric performance. Figure 2.3 provides a schematic depiction of the photoelectric effect (Khan and Gibbons, 2014).

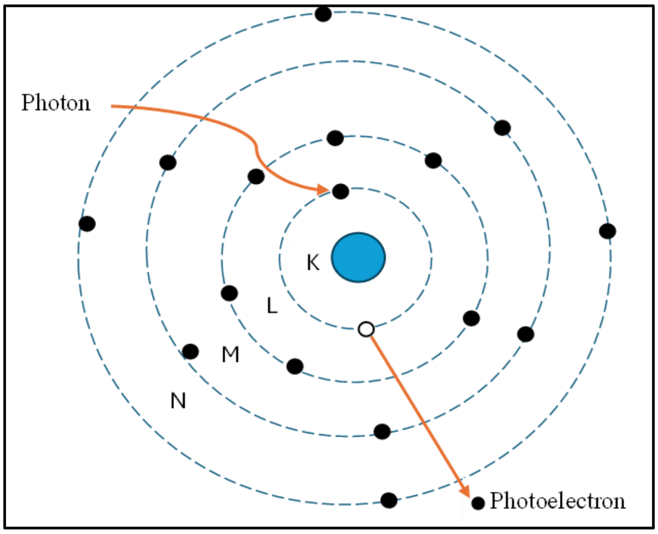

Figure 2.3 Schematic diagram for photoelectric interaction (Khan and Gibbons, 2014).

2.3.3 Compton scattering

Compton scattering dominates at intermediate photon energies, where photons transfer part of their energy to loosely bound electrons, resulting in scattered photons and recoil electrons (Ziessman et al., 2006). While Compton interactions contribute to overall energy deposition, their effect on TL efficiency is relatively indirect, as the scattered electrons are less likely to be captured in the metastable traps responsible for luminescence. Experimental studies in thin-film oxides suggest that Compton events primarily influence bulk energy deposition rather than specific trap population dynamics. Figure. 2.4 illustrates Compton scattering, showing the interaction between the incident photon and electrons.

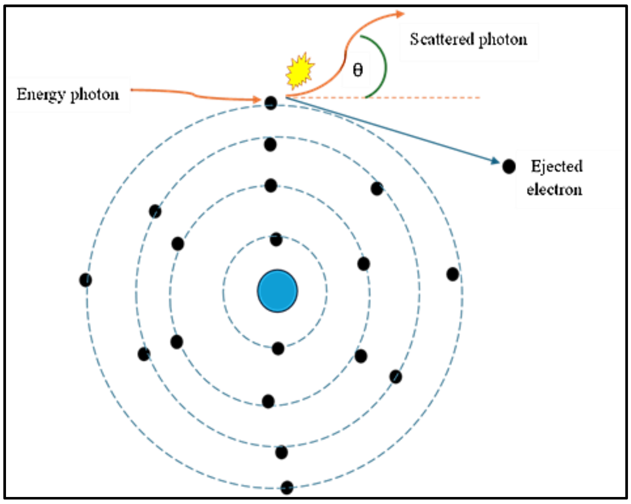

Figure 2.4 The schematic diagram for Compton interaction (Khan and Gibbons, 2014).

2.3.4 Pair production

Pair production (Figure 2.5) becomes significant only at photon energies above 1.02 MeV, where photons interact with the nuclear field to produce electron–positron pairs (Tuchin, 2010; Khan & Gibbons, 2014). For most practical TL applications, diagnostic X-rays, therapeutic gamma rays, or beta sources, pair production is negligible. Consequently, its contribution to trap formation in $TiO_2/Cu/TiO_2$ multilayers is minimal.

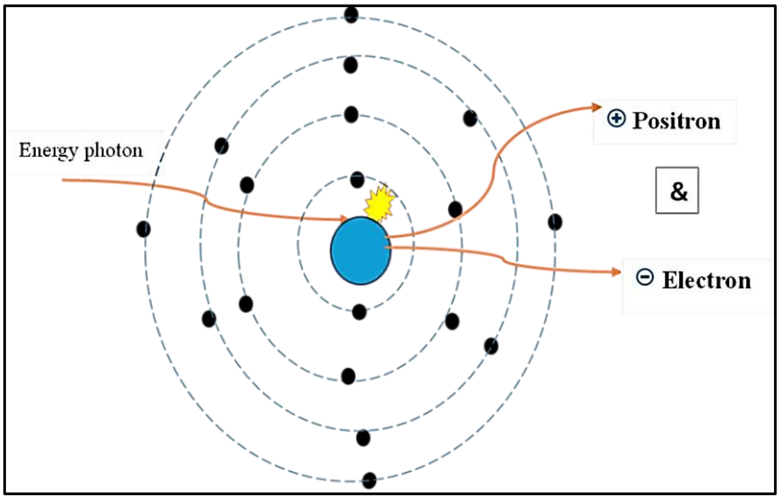

Figure 2.5 Pair the production interaction schematic exhibiting annihilation radiation (Khan and Gibbons, 2014).

2.3.5 Relevance to TL materials and thin films

Taken together, the literature indicates that the photoelectric effect is the primary interaction mechanism underlying TL dosimetry, directly linking photon absorption to charge trapping and luminescence emission. Understanding how photoelectric absorption interacts with material defects allows researchers to optimize multilayer TiO_2/Cu/TiO_2 films for enhanced TL response. Manipulating layer thickness, defect density, and dopant concentration can tune absorption efficiency and trap occupancy, providing tailored dosimetric performance under specific radiation sources (Rahman et al., 2020). Compton scattering and pair production, while relevant for general energy deposition, have a secondary or negligible role in the direct operation of TL detectors

2.4 Applications of thermoluminescent dosimeters (TLDs)

Thermoluminescent dosimeters are widely used in personal, clinical, environmental, and radiotherapy dosimetry due to their high sensitivity, tissue equivalence, and reproducibility. Early work by Daniels et al. (1953) established the feasibility of TL for radiation measurement, and subsequent studies have expanded its application in medical physics, environmental monitoring, and occupational safety (Azorín Nieto, 2004).

2.4.1 Diagnostic radiology

TLDs have been employed to quantify patient doses from diagnostic X-rays, particularly using LiF: Mg, Ti, and tissue-equivalent $Li_2B_4O_7$:Mn phosphors (Rivera-Montalvo, 2016). These studies show that TLDs can accurately map dose distribution in phantoms and patients, providing critical data for optimizing imaging protocols and reducing unnecessary exposure.

2.4.2 Radiotherapy

In radiotherapy, TLDs are used for in vivo and phantom dosimetry, including verification of machine output, beam uniformity, and dose distributions for both internal and external treatments (Azorin et al., 1990). Recent research demonstrates that micro- and nanoscale TL materials can enhance spatial resolution and sensitivity in high-gradient fields, which is particularly relevant for modern intensity-modulated radiotherapy.

2.4.3 Radiation protection and personnel dosimetry

Several studies have validated TLD use for occupational dose monitoring in medical, industrial, and nuclear environments (Murthy & Reddy, 2008). Comparative studies indicate that thin-film and microdosimeter configurations provide rapid, reliable readings while maintaining tissue equivalence (Christensen et al., 1982).

2.4.4 Environmental monitoring

TLDs have been applied in environmental dose assessment using passive detectors such as LiF:Mg,Ti, CaF_2: Mn, and Al_2O_3:C (Ranogajec-Komor, 2002; Mobit & Kron, 2006). Research emphasizes the importance of material sensitivity and detector calibration for detecting low-level radiation in natural and anthropogenic environments.