MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES

MANUFACTURING PROCESS DEVELOPMENT FOR LANTHANUM HEXABORIDE (LaB_6) THIN FILM FILAMENTS

BİSET TOPRAK

MASTER THESIS

Department of Industrial and Systems Engineering

Thesis Supervisor

Prof. Dr. Bahadır TUNABOYLU

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Declaration of Authorship

I, Biset Toprak, declare that this thesis titled, 'Manufacturing Process Development for Lanthanum Hexaboride (LaB_6) Thin Film Filaments' and the work presented in it are my own. I confirm that:

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- Where I have consulted the published work of others, this is always clearly attributed.
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Manufacturing Process Development for Lanthanum Hexaboride (LaB_6) Thin Film Filaments

Biset Toprak

Abstract

Thin films of rare-earth hexaborides (REB_6) are promising for wear and corrosion protective, decorative, and thermionic coatings. Among many hexaborides available, due to its unique properties lanthanum hexaboride (LaB_6) is mostly used as a bright and long life thermionic emission source in electron microscopes. Unlike single-crystal LaB_6 cathodes used today, LaB_6 thin-film coated metal filaments can be advantageous due to their simple design, easy installation, cost-efficient manufacturing, and less energy consumption. In this study, LaB_6 thin films were grown onto tantalum (Ta), molybdenum (Mo), and tungsten (W) wire-substrates using magnetron sputtering (MS). Tape-test was used on the film surfaces to determine the adhesion of the LaB_6 films to the substrates. The morphology, structure, and stoichiometry of tape-tested films were investigated by stereo microscopy, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Stereo microscopy and SEM analysis showed that the films were grown by magnetron sputtering have dense, fine columnar structure without peeling or flaking. From the XPS analysis of LaB_6/W, it was observed that the film was oxidized and there were no peaks of any element other than lanthanum, boron, and oxygen found. The analysis shows that the composition of the film was lanthanum tetraboride (LaB_4) coated over the tungsten (W) substrate at the deposition conditions. In addition to the characterization, the design of thin-film filaments was completed as described in our patent application. Then, the cost analysis including material, labor, machine, and analysis cost, was conducted. As a result of the study, encouraging results for the low cost filament application was obtained.

Keywords: Lanthanum Hexaboride (LaB_6), Thermionic Coatings, Thin Films, Magnetron Sputtering (MS), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM)

Lantan Hekzaborür (LaB_6) İnce Film Filamentler için Üretim Süreci Geliştirilmesi

Biset Toprak

Öz

Nadir toprak hekzaborürlerinin (REB_6) aşınma ve korozyona karşı koruyucu, dekoratif ve termiyonik ince filmleri gelecek vaat etmektedir. Mevcut birçok hekzaborür arasında benzersiz özellikleri nedeniyle lantan hekzaborür (LaB_6) çoğunlukla elektron mikroskoplarında parlak ve uzun ömürlü termiyonik emisyon kaynağı olarak kullanılmaktadır. Fakat günümüzde kullanılan tek kristal LaB_6 katotların aksine LaB_6 ince film kaplı metal filamentler basit tasarımı, kolay kurulumu, düşük fiyatları ve az enerji tüketimi nedeniyle daha avantajlı görülmektedir. Bu çalışmada, magnetron sıçratma sistemi kullanılarak tantal (Ta), molibden (Mo) ve tungsten (W) tel alttaşlar üzerine LaB_6 ince filmler kaplanmıştır. LaB_6 filmlerinin alttaşlara yapışkanlığını belirlemek için film yüzeylerine bant testi uygulanmıştır. Bant testi uygulanan filmlerin morfolojisi, yapısı ve stokiyometrisi stereo mikroskobu, taramalı elektron mikroskobu (SEM) ve X-ışını fotoelektron spektroskobu (XPS) ile analiz edilmiştir. Stereo mikroskobu ve SEM analizi sonuçlarına göre geliştirilen filmlerde soyulma olmadığı ve filmlerin alttaşlara iyi yapışma sağladığı gözlemlenmiştir. LaB_6/W filminin XPS analizi filmin oksitlendiğini ve filmlerde lantan, bor ve oksijen dışında herhangi bir elementin bulunmadığını göstermiştir. Analiz sonuçları, mevcut deney parametreleri altında tungsten teli üzerine kaplanan filmin kompoziyonunun lantan tetraborür (LaB_4) olduğunu göstermektedir. Karakterizasyon çalışmalarına ek olarak ince film filamentlerin tasarımı ve maliyet analizi de yapılmış olup çalışma sonucunda düşük maliyetli filament uygulaması için umut verici sonuçlar elde edilmiştir.

Anahtar Sözcükler: Lantan hekzaborür (LaB_6), Termiyonik Kaplamalar, İnce Filmler, Magnetron Sıçratma (MS), Taramalı Elektron Mikroskobu (SEM), Geçirimli Elektron Mikroskobu (TEM)

I would like to dedicate this work to my parents and to my sisters and brother.

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Abbreviations

A	Peak Area
Ar	Argon
ASF	Atomic Sensitivity Factor
BCC	Body Centered Cubic
CeB_6	Cerium Hexaboride
DCMS	Direct Current Magnetron Sputtering
LaB_6	Lanthanum Hexaboride
Mo	Molybdenum
MS	Magnetron Sputtering
PVD	Physical Vapor Deposition
RF	Radio Frequency
REB_6	Rare-Earth Hexaboride
QCM	Quartz Crystal Microbalance
SCCM	Standard Qubic Centimeters per Minute
SEM	Scanning Electron Microscopy
SiO_2	Silicon dioxide
Si	Silicon
Ta	Tantalum
TEM	Transmission Electron Microscopy
W	Tungsten
XPS	X-ray Photoemission Spectroscopy
2-D	Two Dimensional

Physical Constants

Richardson constant (W)	A	=	$60 \times Acm^{-2}\ K^{-2}$
Richardson constant (LaB_6)	A	=	$30 \times Acm^{-2}\ K^{-2}$
Boltzmann constant	k	=	$1.3807 \times 10^{-23} K^{-1}$

Symbols

Symbol	Name	Unit
J	emission current density	Acm^{-2}
T	temperature	K
ϕ	work function	eV

Chapter 1

Introduction

1.1 Research Background

Boron, the lightest and the only nonmetallic element of III A group in the periodic table, shows interesting properties similar to carbon [1]. Recently, a considerable literature has grown up around the theme of application of inorganic boron compounds as thermionic cathode material [1, 2]. Rare-earth hexaborides (REB_6), characterized by low work function, high mechanical strength, high electron emission, high melting point, low electrical resistivity, low volatility at high temperature, and high chemical resistance, accepted as the best electron emissive materials [3–9]. Among many hexaborides available, lanthanum hexaboride (LaB_6) occupies a unique place as thermionic emitter source due to the combination of low work function, high melting point, high chemical and thermal stability, and low evaporation rate at high-temperature [4, 7, 10–14]. Recently, LaB_6 and also cerium hexaboride (CeB_6) single crystals have been mostly used as a brighter and long-life thermionic emitter than tungsten cathodes in scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [15]. Besides the bulk counterparts, thin films of LaB_6 are promising for wear and corrosion protective, decorative, and thermionic coatings [2, 16–18]. Especially, the application of LaB_6 thin-film coated metal filaments is very promising due to their potential in simple design, easy usage, and low operating energy and low cost with respect to the commercially available single crystal cathodes [18–20]. The thin films can be deposited easily at low temperatures using physical vapor deposition (PVD) methods [12]. PVD method is classified into two categories called sputtering and evaporation. The classification is based on the process

of extraction particles from the target material [21]. However, there are some problems that arise during the evaporation of refractory metals and alloys because of their high melting point. Magnetron sputtering (MS) has emerged to overcome these problems as well as providing the opportunity to deposit denser, adhesive, and smoother films at low temperatures with ease of controlling the parameters [18, 20–24]. Due to the advantages over other PVD methods in film growth and adaptation to industry, magnetron sputtering was preferred in this study for the deposition of LaB_6 thin films.

1.2 Motivation

Turkey has 72% of the total boron mine reserves in the world with 803 million tons. However, there is only 8% of the extracted boron reserves are used domestically and 92% is exported as semi-finished or raw material [25]. Thus, it is very important to develop production technologies to produce boron related semi-finished and finished products and compete with other boron products in the global market. In Turkey, there more than 165 transmission electron microscopes and scanning electron microscopes, mostly used in universities, laboratories, and research centers [26]. Thermionic electron sources that have been used in these microscopes are typically the main consumables in the electron microscopy operational costs due to their high prices and limited service times. Filamentary tungsten, single-crystal LaB_6 and CeB_6 cathodes are imported and their prices are 3.924 TL, 14.569 TL and 42.097 TL, respectively in Turkey that has the largest boron resources in the world provides a motivation for development of high value-added boron products with an innovative approach. For this purpose, domestic production LaB_6 thin-film coated metal filaments are investigated here in this thesis study for the first time in Turkey. With the domestic production of higher quality LaB_6 thin film filaments at a lower price than competitors, it will be possible to encourage boron-based competition and to make new investments in boron related products in Turkey.

1.3 Objectives

The main objective of the thesis was to develop a manufacturing process for LaB_6 thin-film filaments. The specific objectives of this study were as follows:

- To deposit LaB_6 on tantalum, molybdenum, and tungsten substrates by magnetron sputtering (MS)
- To analyze the adhesion of the LaB_6 films to the substrates by using tape-test on the film surfaces
- To investigate the morphology, structure, and stoichiometry of tape-tested films in terms of stereo microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy
- To determine the design of the thin-film filaments.
- To complete cost analysis of the thin-film cathodes

1.4 Organization

This thesis is organized as follows.

- In the first chapter, the general introduction of the research was provided. Then, the motivation behind the work and objectives of the study were explained.
- In the second chapter, literature review about LaB_6 and its properties, application areas were explained. Then, thermionic emitters were introduced, commercially available tungsten and LaB_6 cathodes were compared. After that grow methods for sintered rods, single crystals, and thin film filaments of LaB_6 were explained.
- In the third chapter, our experimental work was provided. In the study, the LaB_6 films were deposited on the tungsten, tantalum and molybdenum substrates using magnetron sputtering system.
- In the fourth chapter, tape-tested LaB_6/W, LaB_6/Ta, and LaB_6/Mo films were characterized by stereo microscope, SEM, and XPS for investigation of their adhesion, morphology and elemental composition. In addition,the result of cost analysis including material, labor, machine, and analysis cost was presented.
- In the fifth chapter, the conclusion and future work were provided.

Chapter 2

Literature Review

2.1 Lanthanum Hexaboride

LaB_6, one of the rare-earth hexaboride, is a refractory ceramic compound characterized by unique properties, which makes it attractive for various applications [1, 4, 7, 11–14, 27–29]. LaB_6 is characterized by low work function, high melting point, high chemical, and thermal stability, low evaporation rate at high temperature [4, 10–14, 27]. The combination of all these unique properties make LaB_6 advantageous for small spot size applications such as photocathodes, high-resolution detectors, resistors, thermionic emitters, and field emitters [2, 30–33]. It is also very promising material for wear and corrosion protective, decorative, and thermionic coatings [16–18].

2.1.1 Physical and Chemical Properties

Among many hexaborides available, LaB_6 hexaboride occupies a unique place as thermionic emitter source due to the combination of low work function, high melting point, high chemical, and thermal stability, low evaporation rate at high temperature [4, 10–14, 27]. It is the highest electron emissive material and its performance is not affected by the existence of either oxygen or nitrogen [5, 34]. As it can be seen in Figure 2.1, it crystallizes in the Body-Centered Cubic (BCC) lattice in which rare-earth metal ion La is positioned at the center of the unit cell and surrounded by the octahedral boron atoms positioned at the corners [8–10, 13, 27, 35]. Also, low work function, low resistivity, and metallic conductivity of LaB_6 are explained by this arrangement of the atoms [8, 13].

The three-dimensional boron framework and covalent bonds between boron atoms in octahedral and between the octahedral of the neighboring cells provide chemical stability, high hardness, high melting temperature [9, 17, 32]. The color of the LaB_6 is purple and blue for stoichiometric composition and boron-rich compositions, respectively [36].

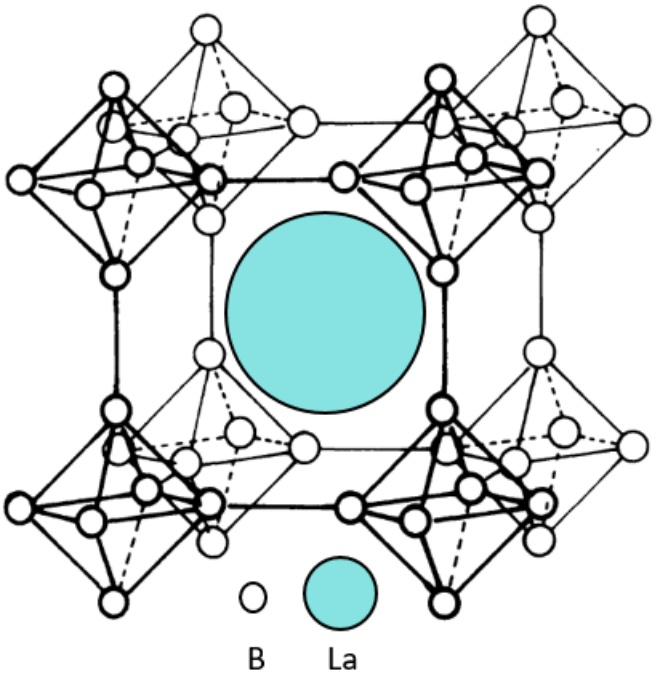

FIGURE 2.1: Lattice structure of LaB_6 modified from [35].

Figure 2.2 shows the binary phase diagram of LaB_6, composed of 86% boron of its atomic weight. It can be seen that LaB_6 melts congruently at 2715° C [15]. It has the highest melting temperature, among the stable La-B compounds [35].

Table 2.1 presents the physical and chemical properties of LaB_6. In general, materials having low work functions have lower evaporation temperatures which cause contamination during long time operations result in a decrease in the service life of the cathode. However, LaB_6 is an excellent cathode material because of its low work function and low evaporation rate at high temperatures. [36–38].

The work function of LaB_6 is effected by the interior B/La ratio [46]. Otani found that the service life of the single crystal cathodes was prolonged by increasing boron content without affecting emission characteristics. Thus, non-stoichiometric boron-rich crystals have a longer service life. Also, it was indicated that control of the composition is effective for the determination of service life [38].

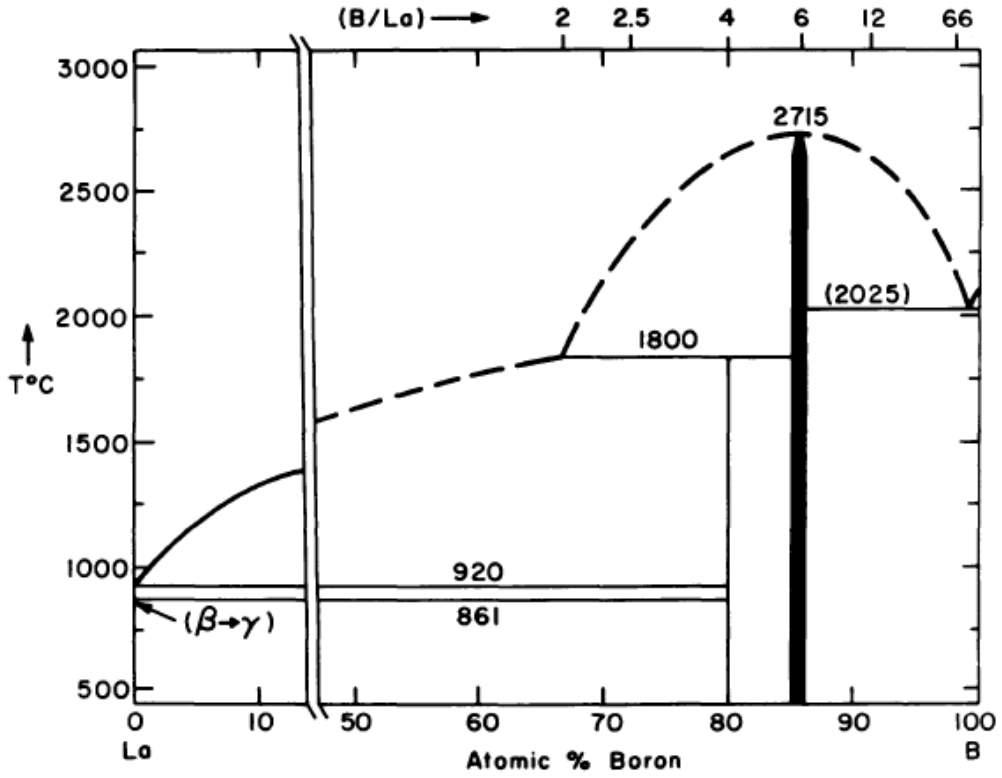

FIGURE 2.2: The La-B phase diagram [35].

2.1.2 Application Areas

LaB_6 single-crystals have been used as bright and long life thermionic emission sources in various electron beam applications such as SEM, TEM, and X-Ray microanalysis [14, 31, 38, 43]. Due to the combination of unique properties, LaB_6 gives advantages in small spot size applications [7]. It also used for photocathodes, high-resolution detectors, resistors, thermionic emitters, and field emitters [2, 30–33]. Besides, thin films of rare-earth hexaborides are promising for wear and corrosion protective, decorative, and thermionic coatings [2, 16–18]. LaB_6 is very attractive for decorative hard coatings applied on luxury accessories due to its purple-red color spectrum, high hardness, and high chemical stability [16–18]. Besides, application of LaB_6 thin-film coated metal filaments are very promising due to their potential in simple design, easy usage, and low operating energy and low cost with respect to the commercially available single crystal cathodes [18–20]. Waldhauser found that LaB_6 and CeB_6 are the most promising compounds for utilization as coated cathodes but the highest electron emission was yielded from LaB_6 coated filament [34]. Recently, LaB_6 thin film cathodes are used in display panels [5].

TABLE 2.1: Physical and chemical properties of LaB_6 [4, 10, 31, 35, 39–45].

Properties	**Unit**	**Value**
Stoichiometry	N/A	6
Molecular Weight	$g.mol^{-1}$	203.78
Theoretical Density	g/cm^{-3}	4.72
Lattice Constant	Å	4.145
Melting Temperature	^oC	2210-2715
Work Function	eV	2.66
Richardson Constant	$A/cm^2.K^2$	30
Thermal Conductivity	W/m.K	110-147
Electrical Resistivity	$\mu\Omega.cm$	15-120
Coefficient of Thermal Expansion	$10^{-6}/K$	6.2-6.4
Hardness	HV	2070-2825

By further investigations, the applications of LaB_6 thin films may be extended to sensors and photocathodes [14].

2.2 Thermionic Emission Sources

Thermionic electron sources gain enough energy to overcome the work function of the cathode material and create electrons at sufficiently high temperatures [47, 48]. The current density (J) of the thermionic emitter is expressed by Richardson - Dushman equation:

$$J_c = AT^2 exp\Big(-\frac{\phi}{k_B T}\Big) \tag{2.1}$$

where A, ϕ, and T, k represents mean effective Richardson constant or the emission constant, work function, emission temperature, and Boltzmann constant, respectively [7]. Thermionic emission is determined by two physical properties, work function, and Richardson constant of the cathode material. Materials with high work function need

high temperature and thus, consume more power to create desired electron current [7, 47, 48]. According to the equation, it can be noted that materials with highest Richardson constant, lowest work function, and higher melting point are desirable as a thermionic emitter [4, 7, 40, 47, 48]. Figure 2.3 shows the relationship between temperature and service life of the cathode. Since thermionic electron sources provide electrons when they heat the current density is proportional to the operating temperature [49]. However, the service life of the source will be decreased with the evaporation and for the best lifetime and stability, the operating temperature should be as low as possible and for T values less than 2000 K, the work function is the primal factor for determination of the current density [40, 49].

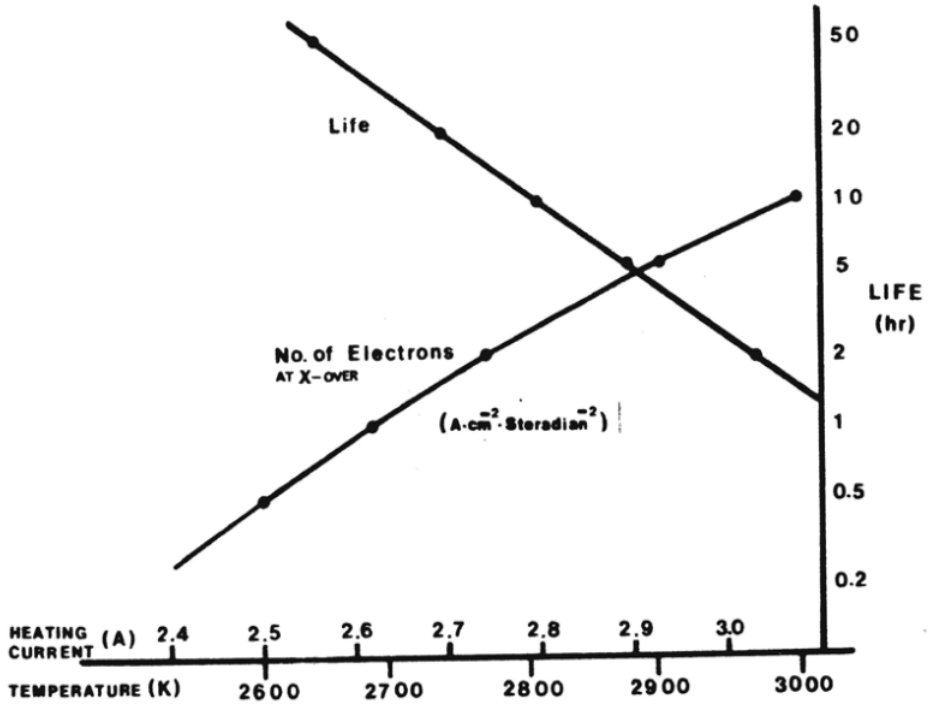

FIGURE 2.3: The relationship between temperature and service life of thermionic emitters [49].

2.2.1 Tungsten Cathodes

Tungsten is the most used metal in thermoemissive applications due to its high emissivity, high thermal and chemical stability. Tungsten based cathode materials have been used in electron guns, electron microscopes, and plasma generators [50]. Figure 2.4 shows a commercially available tungsten cathode structure that consists of hairpin filament (0.1 mm in diameter) with a v-shaped tip. It has a work function of 4.5 eV and an

operating temperature of 2700 K. The service time of the cathode is between 30-100 hours. Except its low price, tungsten cathodes has several disadvantages that can be listed as higher work function, higher operation temperature, and shorter service time than LaB_6 cathodes [48].

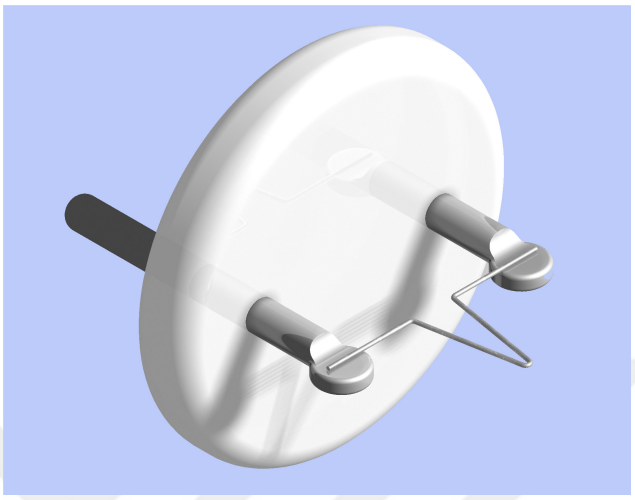

FIGURE 2.4: The image of commercially available tungsten cathode [51].

2.2.2 LaB_6 Cathodes

In literature, LaB_6 cathodes were grouped into 2 categories: indirectly heated and directly heated. While indirectly heated LaB_6 cathodes include pressed, sintered rod and single crystals, directly heated LaB_6 cathodes include LaB_6 coated metal filaments such as tungsten, molybdenum, and rhenium [19, 20]. Figure 2.5 shows the commercially available LaB_6 cathode consists of hairpin filament which indirectly heats the single crystal to create thermionic emission [52]. Single crystals with <100> crystal orientation are most preferable for electron microscopes [46, 53]. LaB_6 cathodes provide longer service time and higher brightness than tungsten cathodes due to their lower operating temperature (1800 K) and low work function (2.66 eV) [48].

2.2.3 Comparison of Tungsten and LaB_6 Cathodes

Performance and lifetime of the cathodes are affected by operating temperature, tip shape, mount design, impurity level, and crystal orientation [45]. Thus, it is very important to optimize these parameters. In practical cathode applications, high purity and sharp tip are required [54]. Besides, the design of the cathode tip is an important



FIGURE 2.5: The image of commercially available LaB_6 cathode [52].

factor for long service time and optimum performance. For thermionic emission sources, small emitter diameters give better performance and resolution and performance. The comparison of tungsten and LaB_6 cathodes are given in Table 2.2. From the table, it can be noted that LaB_6 cathodes are superior to tungsten cathodes in terms of brightness and service life. LaB_6 cathodes have more than 1000 hours in continuous operation while it is 30-100 hours for tungsten. Since operating temperature is one of the factors that affect service life, LaB_6 cathodes are advantageous for longer lifetime. Although the operation temperature of LaB_6 is less than tungsten, it gives higher current density and 10 times greater brightness. The work function values are 2.6 eV and 4.5 eV for LaB_6 and tungsten, respectively. Also, with having small crossover size LaB_6 gives improved coherency [48]. However, LaB_6 cathodes, with various tip shapes (round, flat, sharp) and cone angles have a complicated design and high cost compared to tungsten cathodes [20, 45].

TABLE 2.2: Comparison of LaB_6 and W cathodes [45, 48].

Properties	**LaB_6**	**Tungsten**
Brightness ($A/cm^2.sr$)	10^7	10^6
Typical Service Life (hr)	1000+	30-100
Work Function (eV)	2.70	4.5
Operating Temperature (K)	1800	2800

2.3 Studies on LaB_6 Cathodes

In literature, LaB_6 cathodes have been prepared in various forms such as single crystals, sintered rods, and thin films for utilization as a thermionic electron emitter. A considerable amount of literature has been published on the single-crystal growth of LaB_6. However, due to the promising properties, thin films of LaB_6 need more attention to develop more useful electron emitters. In this section, production methods for LaB_6 single crystals, sintered rods and, thin film filaments were introduced. The cathode types and production methods were summarized in Table 2.3.

TABLE 2.3: Summary of the production techniques of LaB_6 thermionic emitters

Cathode Type	**Method**	**References**
Sintered Rod	Pressing and Sintering	[10, 28, 39, 55, 56]
Single Crystal	Floating Zone	[15, 38, 46, 53, 57–63]
	Molten Salt Electrolysis	[64, 65]
	Chemical Vapor Transport	[54]
	Aluminum Flux	[30, 66, 67]
Thin Film	Electrophoretic Deposition	[3, 19, 68]
	Electron Beam Evaporation	[69]
	Thermal Evaporation	[70, 71]
	Magnetron Sputtering	[4, 11, 20, 34, 72, 73]
	Pulsed Laser Deposition	[14]

2.3.1 Sintered Rod Cathodes

Since powders of LaB_6 has brittle and ductile nature, their conversion into the compact, dense parts is needed. To prepare solid cathode structure in the desired shape from powders, pressing and sintering in vacuum were applied [10]. Sintering with hot-pressing was found the most appreciated method to prepare cathode materials from the powders [39]. Polycrystalline LaB_6 rod cathode, shown in Figure 2.6, was first designed by Broers by

sintering for the utilization in electron microscopes as a brighter and long-life alternative to the tungsten cathodes after the investigation of superior electron emission properties of LaB_6 by Lafferty [10, 55]. It was found that LaB_6 cathodes are superior to tungsten cathodes in terms of brightness, service life, and mechanical stability. The higher brightness than tungsten was explained by lower operating temperature and sharper tip of LaB_6 than tungsten cathodes [55].



FIGURE 2.6: The rod LaB_6 cathode was designed by Broers [55].

However, it was noted that rod cathodes had some difficulties because of having a complex structure, needing higher heating power, and requiring better operation vacuum than tungsten [55, 56]. Additionally, several difficulties arise with uniform heating and determination of the temperature when sintered cathodes are used [10]. It results in irregular emission patterns resulting in low performance in electron microscopes [53]. Sintered rod LaB_6 cathodes has a high cost and poor properties which limit the usage as a cathode material. Also, their preparation is difficult because of requiring a long holding time (2-10 hours) and high sintering temperature (1900-2100 °C) [28].

2.3.2 Single Crystal Cathodes

In literature, floating zone [15, 38, 46, 53, 57–63], molten salt electrolysis [64, 65], chemical vapor transport [54], and aluminum flux [30, 66, 67] methods were used in order to prepare single crystals of LaB_6. Among these methods, the floating zone was mainly used to prepare single crystals with high purity and large size [15, 46, 53, 57–63]. The quality of the crystals is very important to produce thermionic emitters with high reliability and low cost [15, 62]. The performance of the single-crystal LaB_6 cathodes is affected by work function, design of the tip, purity of the emitting area, and the emitter surfaces

[53]. Since high purity and sharp tips are desired properties from a thermionic cathode it is very important to grow single crystals with a sharp tip to increase electron beam current [50, 60]. In general, single crystals with <100> crystal orientation are most preferable because of having the lowest work function [46, 53]. However, it is difficult to grow LaB_6 crystals with suitable size and high purity because of the high melting point, high reactivity, and dissociation of melted compounds [58, 60, 64, 66, 74]. Since LaB_6 is a brittle and hard material, sharpening is difficult process. Thus, the desired shape should be achieved during single crystal growth [12, 39, 54]. In addition, higher temperatures, above 1000 ^{o} C, are needed for crystal growth due to the three-dimensional framework formed by covalently bonded boron atoms [9, 58, 65]. This method can be difficult for the materials having an incongruent melting point [9].

In general, there are several disadvantages of indirectly heated cathodes, single crystal and sintered rod cathodes, pointed in the literature. Sintered rod cathodes complicate the design and require more power than tungsten cathodes. Besides, single crystals are expensive than tungsten cathodes and both of them are fragile [19, 20]. Firstly, new and simple design for the directly heated filament in rectangular and circular shape mounted on graphite holders was introduced by Leung by cutting from bulk material using a diamond saw [41].

2.3.3 Thin Film Cathodes

In literature, thermionic emission properties of indirectly heated rare-earth hexaborides as single crystal or sintered rod of LaB_6 investigated mostly. Because of brittleness, more energy consumption, and high price of the indirectly heated cathodes, LaB_6 thin film cathodes seems very attractive [12, 19, 20]. Two dimensional (2-D) nanostructures called thin films show superior properties than bulk counterparts due to having higher aspect ratio, smaller size and larger surface area [1, 75]. However, there are few studies related to thin films for the utilization of thermionic cathode material. In literature, lanthanum hexaboride thin films were grown by electrophoretic deposition [3, 19, 68], thermal evaporation [70, 71], magnetron sputtering [4, 11, 20, 34, 72, 73], electron beam deposition [69], and pulsed laser deposition [14] in order to investigate their electron emission properties and service life.

Buckingham produced directly heated metal filaments by coating rhenium tape with LaB_6 in for ion gauges and mass spectrometers [3]. Favreau cataphoretically coated LaB_6 on rhenium substrates for utilization in ionization gauges and mass spectrometers. The thickness of the coating was 0.025 mm [68]. Then, the first study in order to investigate the utilization of coated cathodes in electron microscopes was conducted by Khairnar and Mahajan [19]. In their study, LaB_6 was deposited on tantalum filament by electrophoretic deposition. The work functions found between 2.6-2.8 eV. Before deposition, the tantalum wire in hairpin shape was carburized in order to prevent diffusion of boron into the wire. It was found that LaB_6 coated tantalum filaments can be operated at 1873 K while uncoated tungsten filaments need a higher temperature than 3020 K at constant emission density of 8 $A.cm^{-2}$. The lifetime of the filaments was found 55 hours. Since the service life of the cathodes is affected by operating temperature, coated filaments were suggested. It was found that the service life of filaments is primarily determined by the adhesion of LaB_6 to the substrate.

However, the coatings produced by electrophoretic deposition annealed, and directly heated were porous and poor in adhesion. In addition, they were fragile and durable only a few thermal shocks. Besides, the preparation of coatings by electrophoretic deposition is difficult because heat treatments are required before and after the deposition [20, 34]. Since LaB_6, chemically reactive material, carburizing, boronizing, or nitriding is needed in order to prevent interstitial diffusion of boron atoms [39]. Rhenium, tantalum carbide, and graphite are good alternatives as a base metal since they do not allow diffusion of boron atoms [10, 41, 68].

Since the adhesion of the LaB_6 thin films is one of the main factors that affects service life, Mroczkowski used radio frequency (RF) magnetron sputtering to deposit adherent LaB_6 thin films on tungsten. As a result, adherent, and stress-free thin films with 1 μm thickness were obtained. Work function and electron emission values were found to be consistent with results obtained from bulk LaB_6. The lifetime measurements were carried out at 1200K and measured as more than 1000 hours. The work function of the films was between 2.4-2.6 eV. The surface of the films contained lanthanum oxide (La_2O_3) in addition to LaB_6 [20].

Yutani et al. used e-beam deposition to grow LaB_6 films on tilted angles of 45° and 80° degrees and at temperatures of 300, 750, and 1000 K to investigate the effects of

deposition parameters on physical properties. It was observed that there is a minor effect of substrate temperature on work function. The thermionic emission method was used to investigate electron emission properties at 1300 K and found 10 A.cm^{-2}. The work function of the films had values of 2.7-2.8 eV. However, the films were not stoichiometric because B/La ratio was 5 [69].

In the study conducted by Kinbara et al. LaB_6 thin films have a thickness between 0.2-0.3 μm were deposited on glass by DCMS. They investigated the effect of argon pressure on the composition of the films. It was stated that argon gas has a great influence on the composition of the films. Stoichiometric films were obtained when argon pressure was less than or equal to 2.5 Pa. But it may cause the production of <111> plane which has a high work function. However, under the deposition of 25 Pa argon pressure B/La ratio decreased to 4. It was found that (100) plane films, which are preferable as thermionic emitter due to their low work function can be obtained under an argon pressure of 1 Pa [72].

Oshima et al. evaporated LaB_6 on tantalum substrates for 3 hours. Thin films evaporated at temperatures between 1600- 2200 were mostly stoichiometric. The service time of the cathodes was measured as more than 40 hours at 2200° C. The work function of the cathode was measured as 2.61 $\pm$ 0.05 eV [70].

In the study conducted by Waldhauser et al., DCMS was used to coat the molybdenum and tungsten sheets. After determining the optimum of deposition parameters, the work function was found as 2.8 eV. It was investigated that coated tungsten filament, has the same electron emission current with uncoated one, has nearly 1000° C lower operating temperature [4].

Waldhauser et al. grew thermionic coatings on molybdenum and tungsten substrates by using LaB_6, CeB_6, SmB_6, and YB_6 targets and direct current magnetron sputtering (DCMS). It was observed that all films were over stoichiometric. However, with the increasing pressure of argon B/ La ratio was decreased from 6.7 to 6.3. Among the rare earth elements used in the study, LaB_6 and CeB_6 were found as the most promising ones for utilization as coated cathodes. However, the highest electron emission was yielded from LaB_6 coated filament. Waldhauser et al. stated that physical vapor deposition methods are capable of producing denser, adhesive, and smoother films [34].

Ishii et al. grew LaB_6 on silicon dioxide (SiO_2) film deposited on silicon (Si) substrate by rotation magnet sputtering. They investigated the effects of coating parameters on the work function of the thin films. They used nitrogen-doped target materials, prepared by hot pressing, having different oxygen and nitrogen concentrations, and found that amount of nitrogen and oxygen in target material have a significant effect on the quality of the thin film. The lowest work function of 2.4 eV was measured from the films with <100> crystal orientation by deposited using the sputtering target which has 0.4% nitrogen and less than 1% oxygen. Also, the highest electron density and electron mobility were observed under these circumstances [76].

Nagaoka and Ohmi prepared N- doped LaB_6 films having 20 nm thickness by RF magnetron sputtering It was observed having with having low work function, as well as high chemical stability, application of N-doped LaB_6 films, are promising for thermionic cathodes [73].

Overall, these studies illustrate that several drawbacks, such as high film stress, poor adhesion, short service time, may occur in the production of thin-film filaments [12, 27]. However, the drawbacks may be overcome by well understanding of application-related properties such as microstructure, mechanical properties, and deposition conditions [12, 34]. The growth mechanism including the surface properties of the substrate and composition of target material have a crucial effect on the morphology and structure of the thin films. Thus, it is very important to control and optimize deposition parameters [29, 77]. Mitterer et al. stated that rare-earth hexaborides can be deposited easily at using PVD methods at low temperatures in the fine-grained or amorphous state [12].

Chapter 3

Experimental Work

3.1 Materials

In the study, commercially available target material consisting of 99.9% LaB_6 (Diameter: 76 mm and thickness: 10 mm), as well as tungsten, molybdenum and, tantalum wires mostly studied for filament applications were used. (see Figure 3.1).



(a) (b)

FIGURE 3.1: (a) Commercially available LaB_6 disc target. (b) Molybdenum, tantalum, and tungsten wires with a diameter of 1.1 mm, 1 mm and 0.7 mm, respectively.

3.2 Method

PVD method is classified into two categories called sputtering and evaporation. The classification is based on the separation process of particles from the target material [21]. There are some problems that arise during the evaporation of refractory metals and alloys because of their high melting point. Magnetron sputtering has emerged to overcome the problems that occurred in evaporation as well as being capable of producing highly crystallized and pure thin films at low temperatures with ease of controlling elemental composition [20–24]. Thin films deposited by magnetron sputtering have been used widely in aerospace, automotive and mechanical industries in order to enhance performance and service life. The method is capable to produce thin films having the same functionality as thick films produced by other coating techniques [24, 78, 79].

Figure 3.2 illustrates the general working principle of the magnetron sputtering process. In MS, the material called target material, usually prepared by sintering or hot pressing, is deposited on the substrate as atomic-sized particles to form a thin film in a gaseous plasma. The substrates must be cleaned before deposition. MS system which allows to cleaning and deposition of the substrates in the same reactor [12, 21, 80].

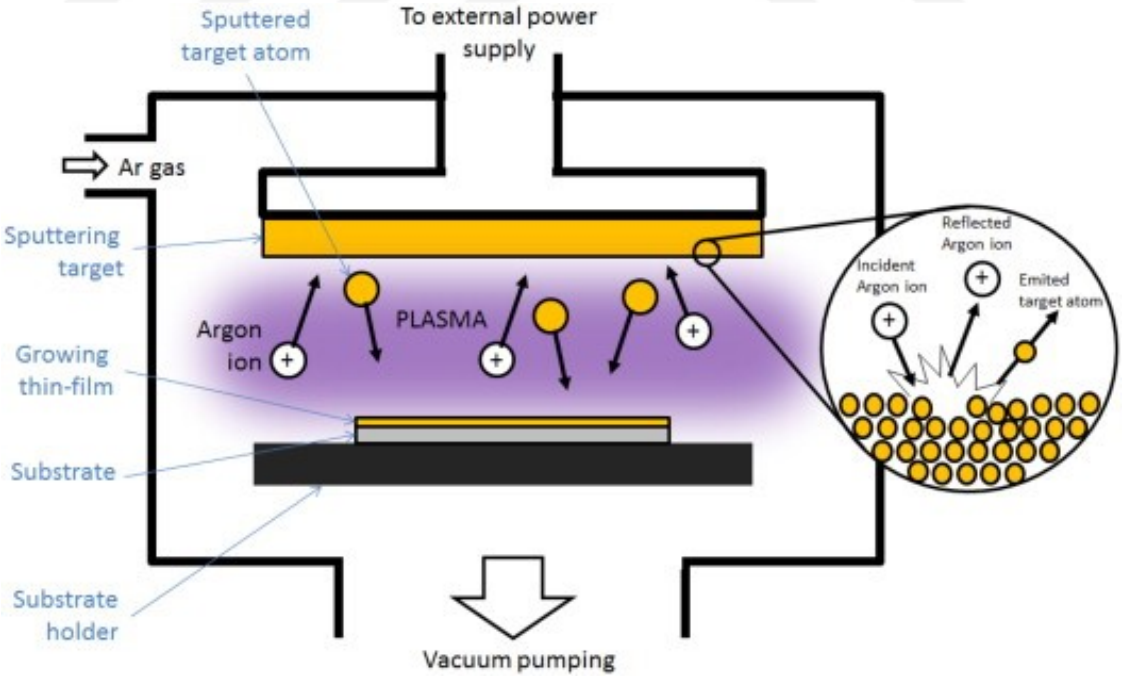

FIGURE 3.2: Schematic illustration of MS System [80].

Magnetron sputtering provides the opportunity to deposit denser, adhesive, and smoother films at low temperatures with ease of controlling the parameters [18, 20, 21] . Due to

the advantages over other PVD methods in film growth and adaptation to industry, magnetron sputtering was preferred in this study for the deposition of LaB_6 thin films. The magnetron sputtering system existing in GTU Nanotechnology Laboratory was used in this study (Figure 3.3). The system is capable of using target materials with diameters of 3 inches and different thicknesses between 1mm - 5mm. Distance between the target material and substrates can be adjusted between 10mm - 100mm. The system includes Quartz Crystal Monitoring (QCM), which can be defined as atomic weighing, which measures the thickness of the films in Angstrom (Å) during deposition. The system allows pre-cleaning before deposition in the same reactor.

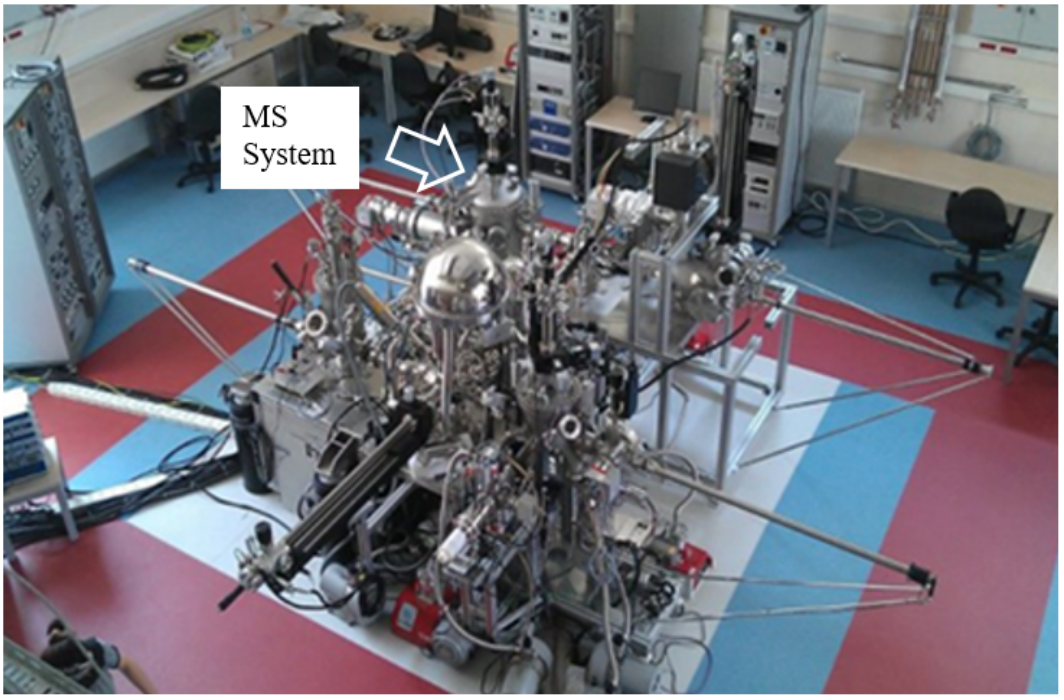

FIGURE 3.3: The Magnetron Sputtering system used in GTU Nanotechnology Laboratory

In the study, the films were sputtered on tungsten, molybdenum, and tantalum wire-based substrates in a magnetron sputtering system using a commercially available disc target. The substrates were cut into pieces with 1.2 mm long. Then, they were cut into lengthwise for obtaining a flat surface. After the wire shaping process, all substrates were placed into the holder shown in Figure 3.4 in order to form thin films under the same conditions, simultaneously.

The holder was placed into the magnetron sputtering system and the distance between the substrates and target material was set 50 mm. Before the deposition, substrate

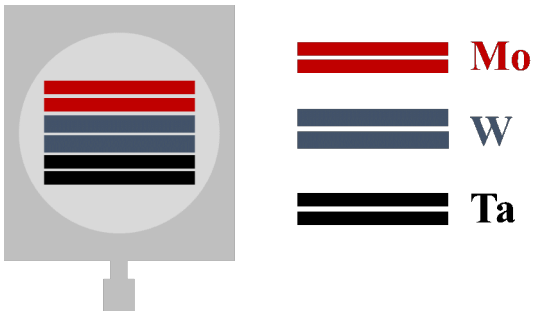

FIGURE 3.4: Schematic illustration of the holder developed.

surfaces were cleaned with 100 W in a vacuum environment in order to remove contaminations and oxides. The films were deposited directly, without using any intermediate layer, on the substrates that were kept at room temperature. Sputtering was carried out under the 2x10^{-3} mbar pressure and 20 W sputtering power with maintaining high purity argon at a flow rate of 3 sccm. The deposition parameters are summarized in Table 3.1.

TABLE 3.1: The coating parameters used in the study

Parameters	
Substrates	W, Ta, and Mo wires
Power	20 W
Thickness	2.5 nm
Sputtering Pressure	2x10^{-3} mbar
Argon Flow Rate	3 sccm
Distance between target and substrate	50 mm
Substrate Temperature	20 ^{o}C

After the deposition, the samples shown in Figure 3.5 were obtained. The thickness of the films was measured in situ by QCM and the deposition was continued until 2.5 nm thickness was reached.

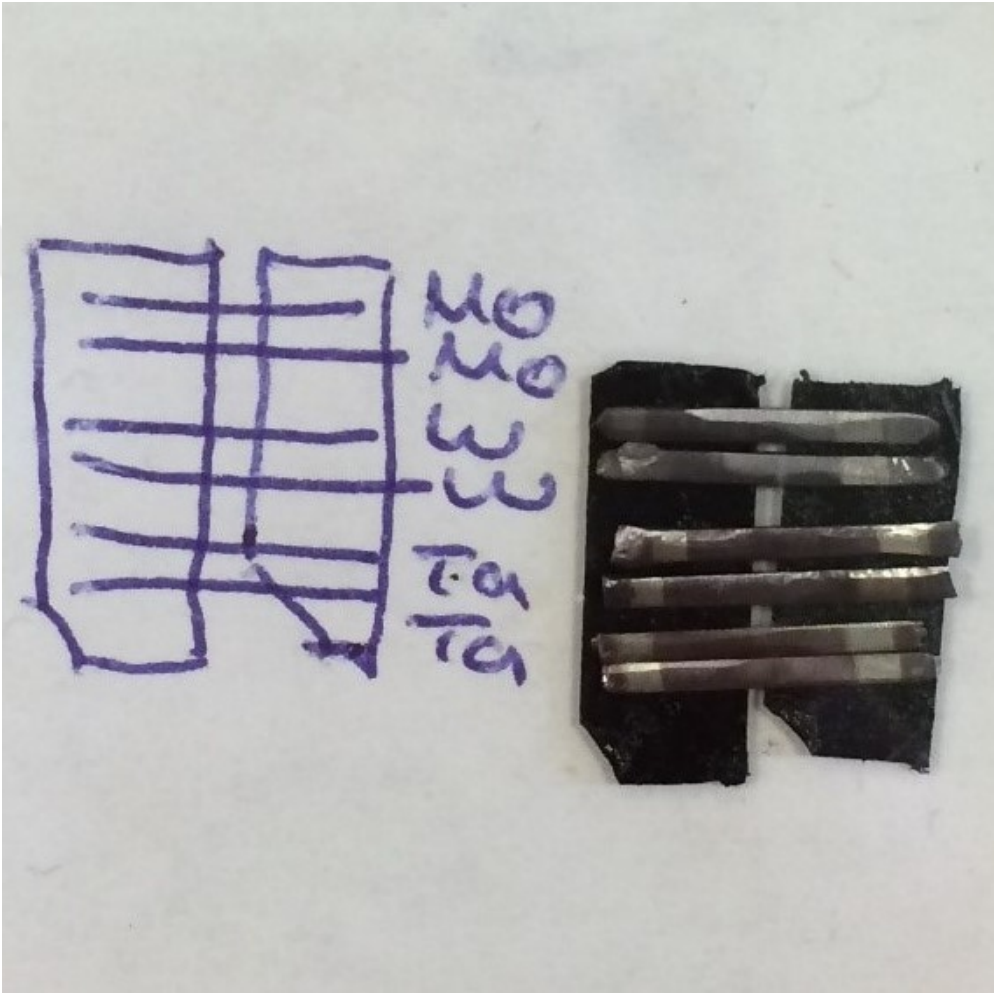

FIGURE 3.5: The image of LaB_6/Mo, LaB_6/W and LaB_6/Ta films, respectively.

Chapter 4

Analysis

4.1 Characterization

Since adhesion is an important factor for the durability of thermionic emitters [19], adhesion of the films to the substrates was investigated by using tape-test on the film surfaces. Then, the morphology, structure, and stoichiometry of tape-tested films were analyzed in terms of stereo microscopy, SEM, and XPS.

4.1.1 Stereo Microscopy

The stereo microscope shown in Figure 4.1 was used to obtain a magnified image of both uncoated and tape-tested film surfaces. The images obtained from the stereo microscopy are presented in Figure 4.2. As shown in the figure there is no peeling or flaking observed after the tape test on the surface of the LaB_6 coated molybdenum, tantalum, and tungsten samples.

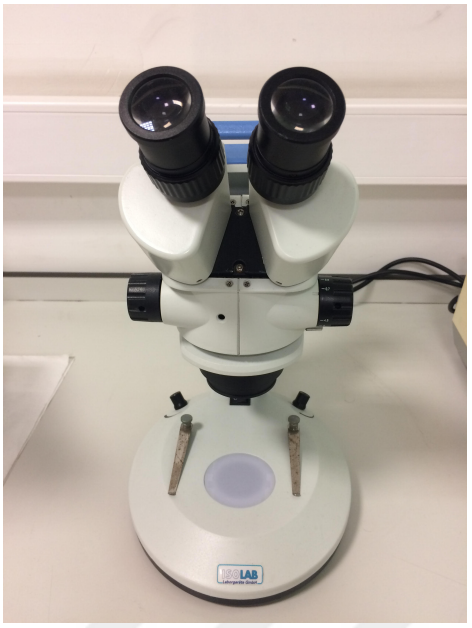

FIGURE 4.1: The stereo microscope used in the study.

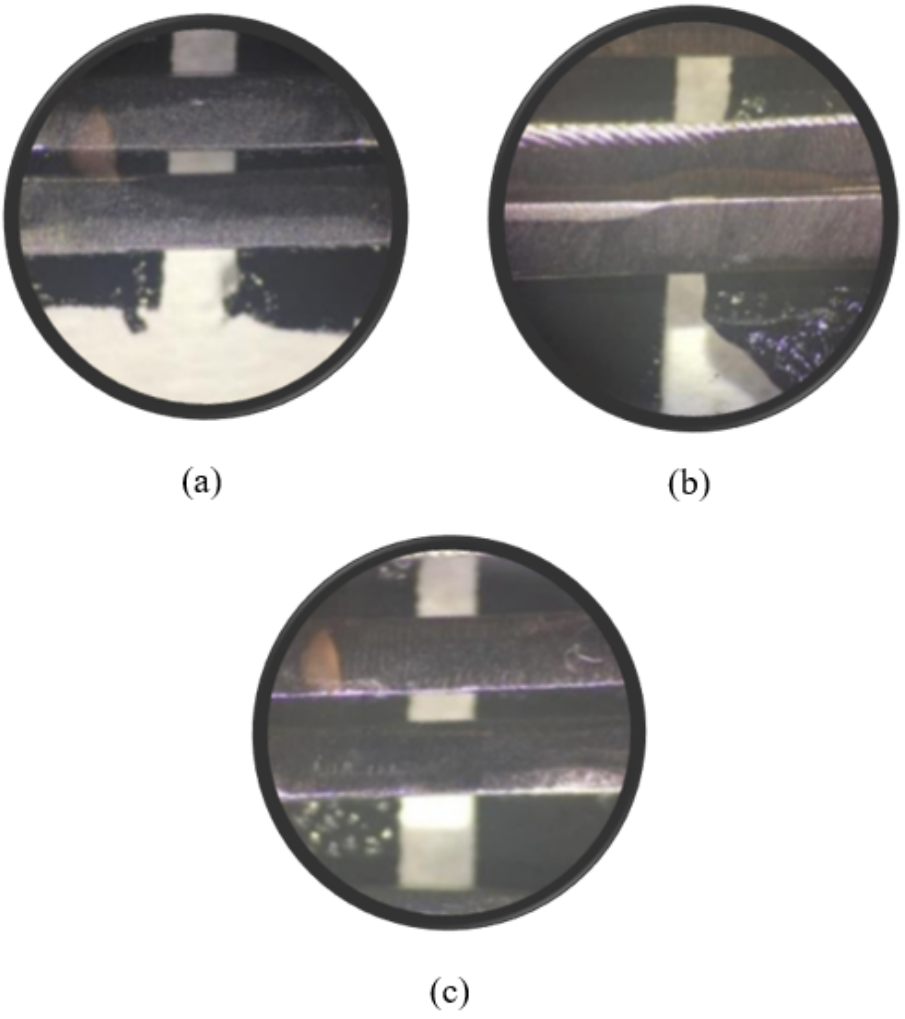

FIGURE 4.2: Stereo microscopy image of tape tested LaB_6 on (a) molybdenum, (b) tantalum, and (c) tungsten with 45X magnification factor.

4.1.2 Scanning Electron Microscopy (SEM)

The morphology of the films was analyzed by SEM. In the analysis, Phenom XL desktop SEM in Istanbul Sehir University was used (see Figure 4.3). The microscope is capable to produce images between 80-100.000x magnification factors.

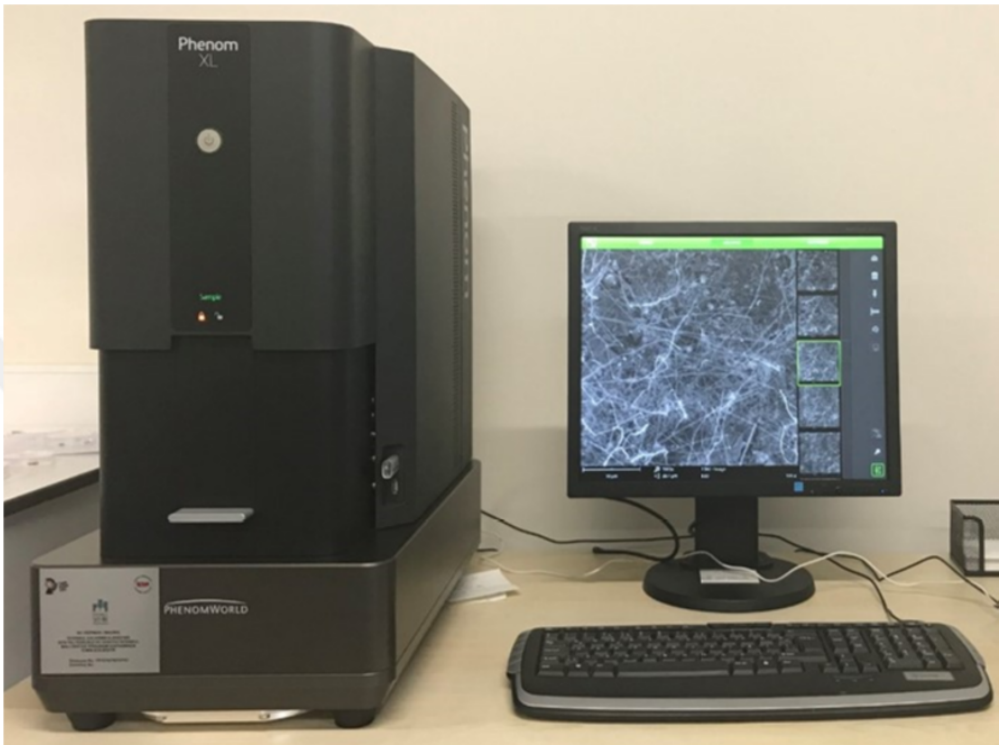

FIGURE 4.3: The SEM used in the study.

Figure 4.4 presents a scanning electron micrograph of uncoated molybdenum, tantalum, and tungsten with a 3000X magnification factor. From the figure, it is apparent that films of LaB_6/W are smoother than those of LaB_6/Mo and LaB_6/Ta. Since the tungsten is the hardest among tantalum and molybdenum, this result is expected because of the wire shaping process.

Figure 4.5 shows the SEM micrograph of LaB_6 film deposited onto molybdenum, tantalum, and tungsten, respectively. Film growth seems to be dense and shows a fine-columnar structure. It can be noted from the SEM analysis films produced by magnetron sputtering are dense and strongly adhered to the wires that will be used as a filament. Since the adhesion depends on the substrate characteristics as well as film properties, good adhesion of the films was partly provided by the cleaning process done before deposition [21].

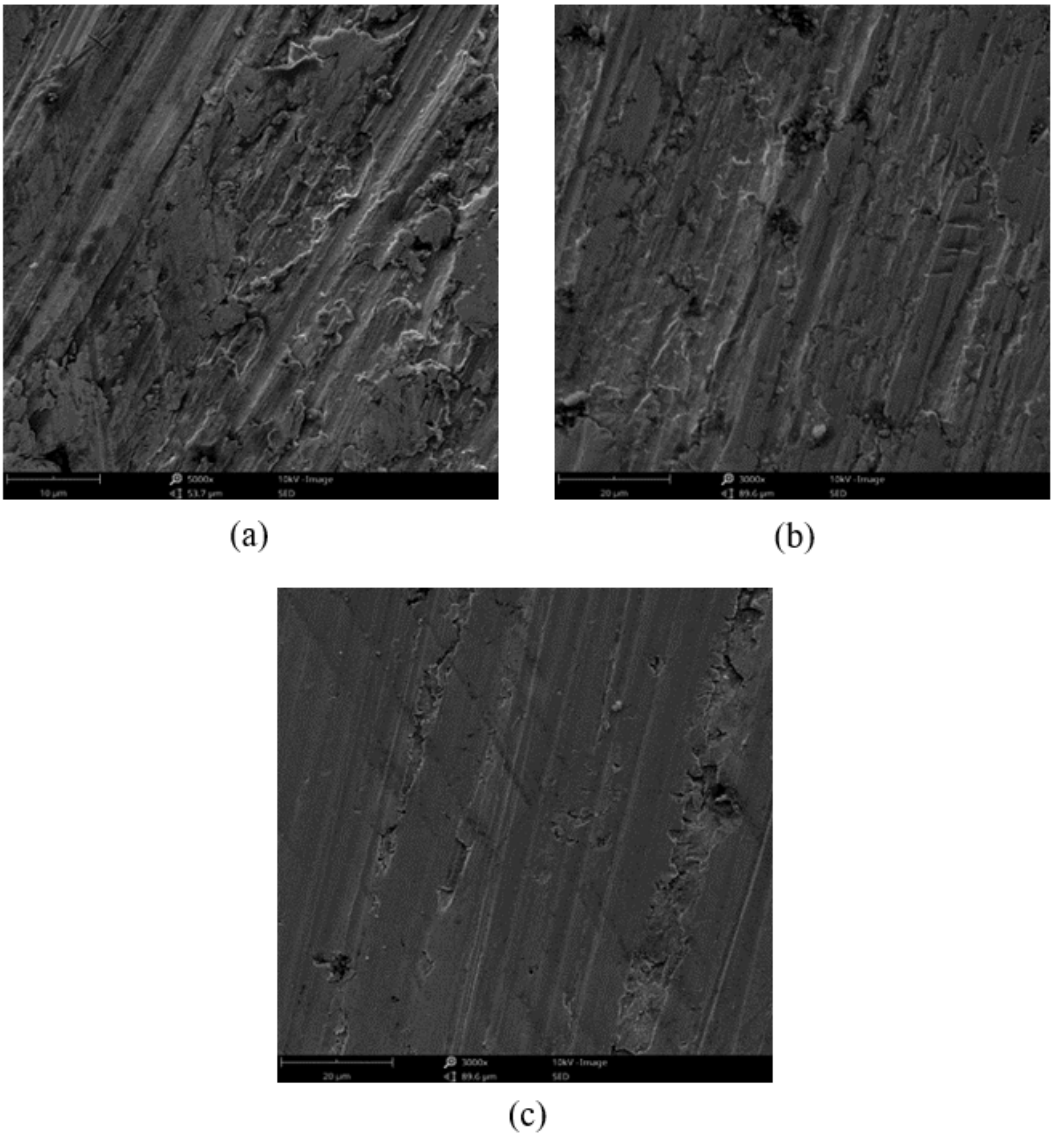

FIGURE 4.4: Scanning electron micrograph of uncoated surface of (a) molybdenum, (b) tantalum and (c) tungsten with 3000X magnification factor.

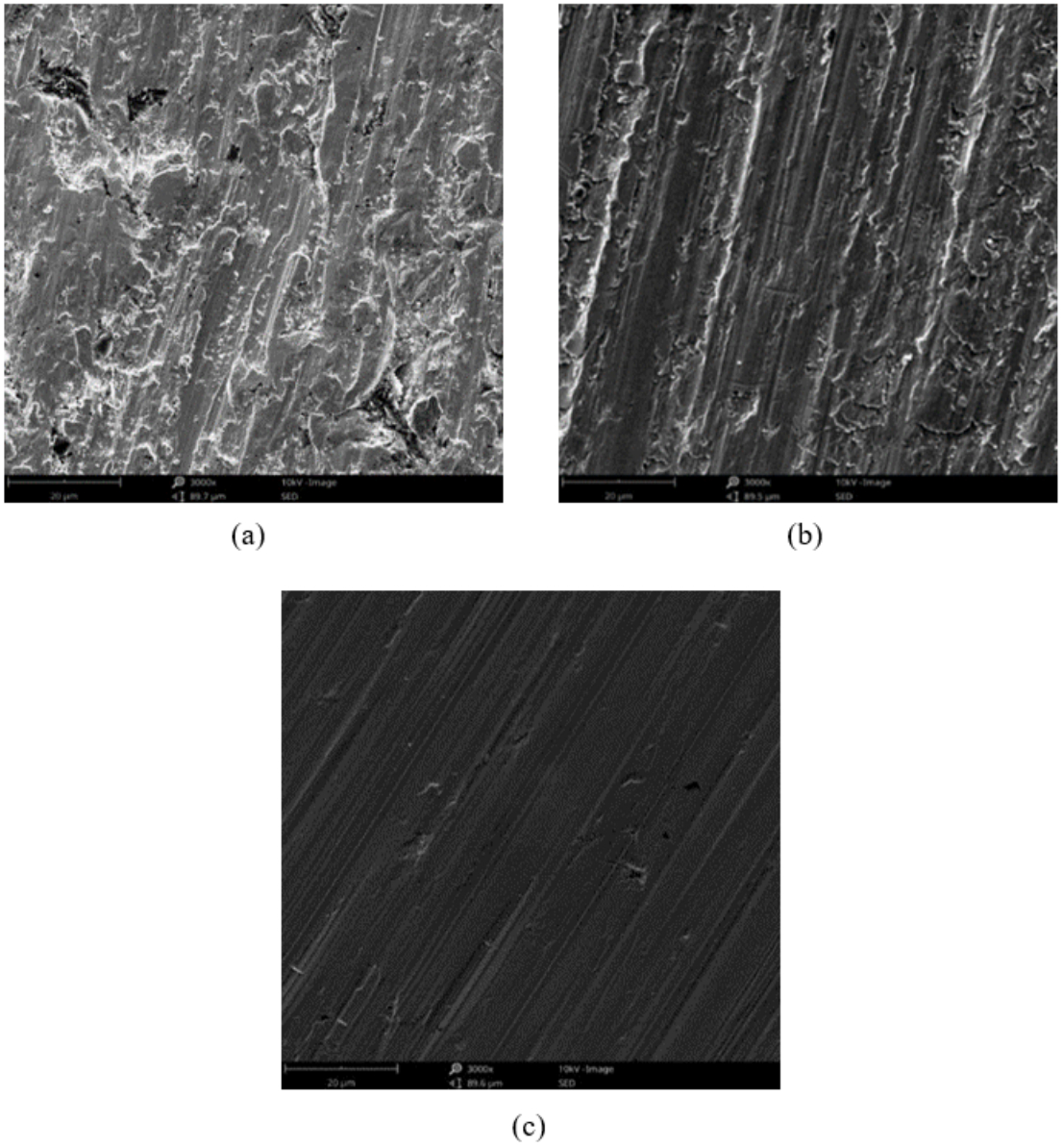

FIGURE 4.5: Scanning electron micrograph of tape tested LaB_6 on (a) molybdenum, (b) tantalum and (c) tungsten with 3000X magnification factor.

4.1.3 X-ray Photoelectron Spectroscopy (XPS)

XPS system in GTU Nanotechnology Laboratory (see Figure 4.6) was used to determine the surface composition and elemental ratios of the LaB_6/W film.

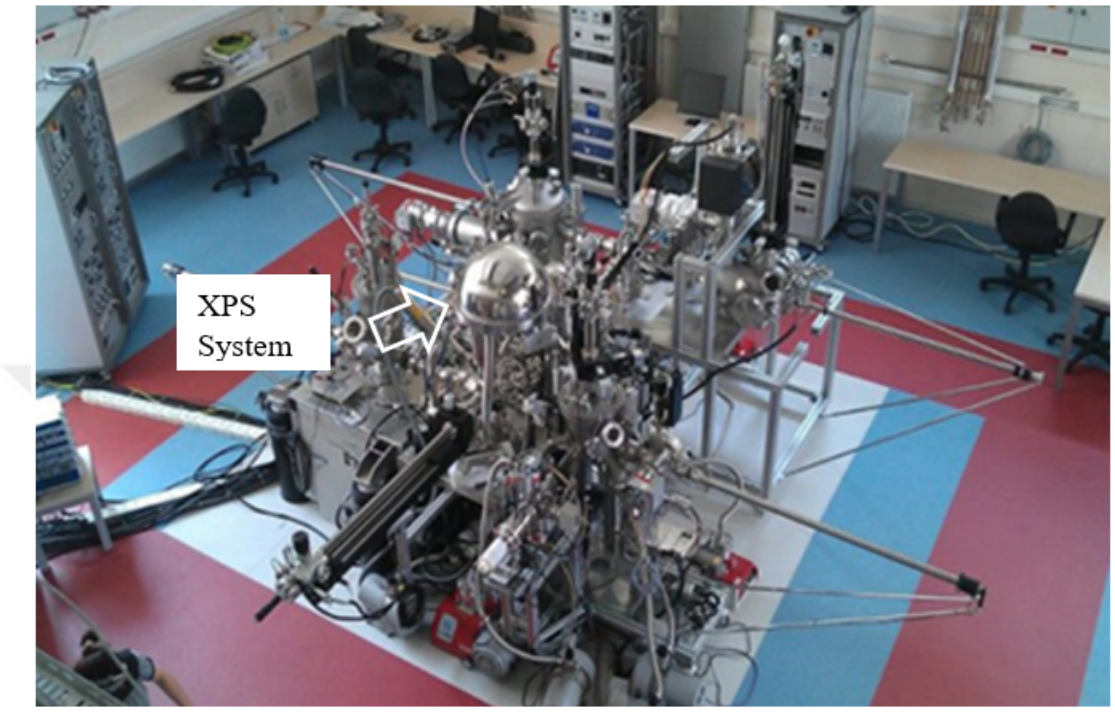

FIGURE 4.6: The XPS system used in the study.

It can be seen from the XPS scan shown in Figure 4.7 the film was oxidized. No peaks of any element other than lanthanum (La), boron (B), and oxygen (O) have been observed on the spectrum.

In order to determine the elemental ratios, the peak area (A) values of La, B and O were determined and divided into the Atomic Sensitivity Factor (ASF), which is specific for each element. Then, the values found for La, B, and O elements were proportioned to each other, and chemical compositions were determined for the samples. The elemental ratios obtained from the XPS analysis are presented in Table 4.1. The analysis shows that the composition of the film was lanthanum tetra boride (LaB_4) coated over the tungsten (W) substrate at the deposition conditions.

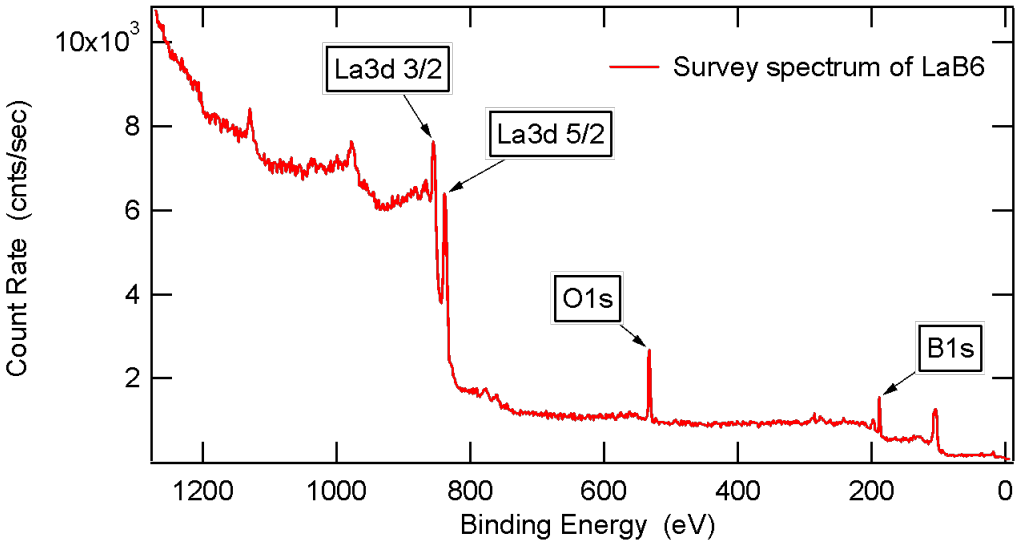

FIGURE 4.7: X-ray photoelectron spectra of the LaB_6/W films.

TABLE 4.1: Elemental ratio calculation of LaB_6/W films

Peak Name	**Peak Area (A)**	**ASF**	**A/ASF**	**%**
O1s	1068,3	0,711	1502,53	28,55
B1s	482,8	0,159	3036,48	57,70
La3d	6602,9	9,122	723,84	13,75

4.2 Cost Analysis

Table 4.2 shows the selling price of filamentary tungsten, single-crystal LaB_6 and CeB_6 cathodes. As can be seen from the table, the prices are quite high when the limited lifetime of the cathodes are considered. In Turkey, there are more than 165 TEM and SEM [26], in which mostly tungsten and LaB_6 cathodes are used as an electron emitter. Because of the advantages over single crystals, in this study LaB_6 thin film filaments were produced for the filamentary purpose by MS. The design of the thin film LaB_6 filaments were described in our patent application (2019-22231). Then, the cost of a filamentary LaB_6 cathode was calculated about 2450 TL by including labor cost, machine cost, analysis cost, and general expenses. The cost factors are listed in Table 4.3. The expected cost of domestic thin film filaments seem quite low comparing with the selling

prices presented in Table 4.2. Besides, the distribution of the cost factors are illustrated in Figure 4.8. As can be seen that the analysis cost forms the 45% followed by machine cost including electricity, maintenance and depreciation expenses. However, the unit cost is expected to decrease when the thin film filaments are produced in batch. As a result of the cost analysis, encouraging results for the lower cost filament application was obtained.

TABLE 4.2: Selling price of filamentary tungsten, single crystal LaB_6 and CeB_6

Cathode Type	**Selling Price / Unit**
LaB_6	14.569 TL (€ 1.592 + VAT
CeB_6	42.097 TL (€ 4.600 + VAT)
Tungsten	3.924 TL (€ 429 + VAT)

TABLE 4.3: Cost factors for a LaB_6 thin film cathode

Cost item	**Cost (TL)**
1. Material	
LaB_6 disc target	0,14
Polyethylene glycol (PEG)	2,89
Argon gas	50,63
Ethanol	3,19
Acetone	2,83
Polyethylene bottle	4,50
Tungsten wire	7,89
Cathode base materials (pins, ceramic disc vs)	100
Total Material Cost	172
2. Labor	
Labor Cost/hour	17,89
Total Labor Cost	53,67
3. Machine	
Electricity	14,30
Maintenance	0,23
Depreciation	692,83
Total Machine Cost	707,36
4. Analyses	
SEM	70
AFM	50
XRD	70
Microhardness	150
XPS	100
XPS depth profiling	100
Nanoindentation	100
Scratch Test	50
Electron emission test	50
EDM (Electrical Discharge Machining)	200,6
Total Analysis Cost (VAT included)	1.109,91
5. Other	408,60
TOTAL COST	**2.451,61**

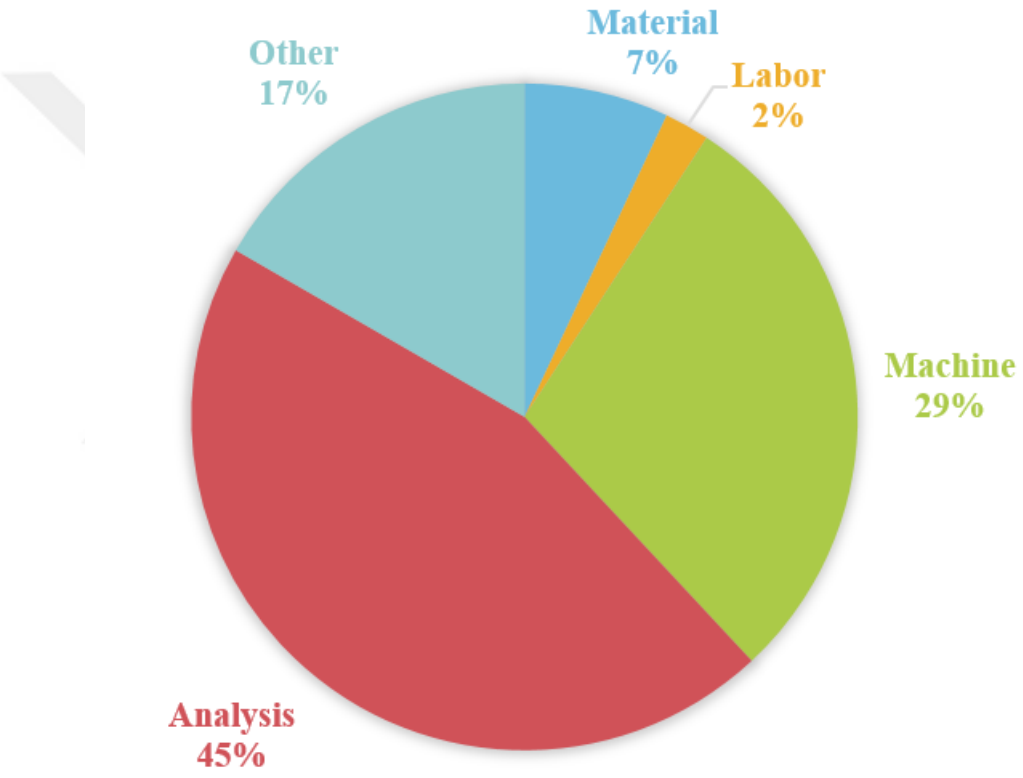

FIGURE 4.8: Distribution of cost factors for a LaB_6 thin film cathode.

Chapter 5

Conclusion and Future Work

5.1 Conclusion

Among many hexaborides, LaB_6 is mostly used as a thermionic electron source that offers high brightness and long life in electron microscopes. LaB_6 is a promising material for decorative, wear and corrosion resistance, and thermionic coatings. The study aimed to perform the deposition of LaB_6 thin films on molybdenum, tantalum, and tungsten wires and investigation of their adherence, morphology, and elemental ratio. To determine the adhesion of the LaB_6 films, tape-test was used on the film surfaces. Then, the morphology, structure, and stoichiometry of tape-tested films were investigated by stereo microscopy, SEM, and XPS. Stereo microscopy and SEM analyses showed that the films were grown by magnetron sputtering have dense, fine columnar structure without peeling or flaking. In the XPS analysis of LaB_6/W film, it was observed that the film was oxidized and there were no peaks of any element other than lanthanum, boron, and oxygen found. The analyses show that the composition of the film was LaB_4 coated over W substrate at the deposition conditions. According to characterization results, the deposition and characterization of LaB_6 films on the metallic substrates were completed. Also, thin-film filaments were designed as described in patent our application (2019/22231). The cost of a LaB_6 thin-film cathode structure was analysed and found about 2450 TL. As a result of the study, encouraging results for the lower cost filament application was obtained.

5.2 Future Work

This study serves as a base of future studies for the domestic production of thin-film thermionic emitters with high quality and low price. However, further experiments are required to produce high-quality films in the desired composition by changing the target composition and magnetron sputtering system parameters. For further studies, LaB_6 target will be segmented to include a boron content to have stoichiometric films. After determining the optimal parameters, electron emission properties, and service life measurements of the samples will be investigated to develop a full manufacturing process for thin-film filaments for electron microscopes.

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