

**Growth and Characterization of Chromium Oxynitride
Thin Films by RF Magnetron Sputtering for Energy
Harvesting and Energy Storage Applications**

BY

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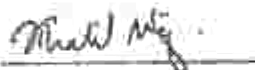
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Dedication

My dedication goes to Allah for his infinite mercies upon me to have concluded my study. The journey was not easy from the start, but His guidance and favor enabled me to surmount the rigorous and challenging period. I thanked Him for the provisions He bestowed upon me and acknowledged His favor. Certainly, He Hears and Sees all affairs.

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Lastly, I dedicate this thesis to my loving, caring, and supportive family, especially my children A'isha and Abdullah, I appreciate their patience for absenteeism during the period of study.

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TABLE OF CONTENTS

ACKNOWLEDGMENTS	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS.....	xi
ABSTRACT.....	xii
ملخص الرسالة.....	xiv
CHAPTER 1 INTRODUCTION	1
1.1 Transition Metal Nitride.....	1
1.2 Chromium Nitride	2
1.3 Chromium Oxide and Oxynitride.....	3
1.4 Thesis Objective.....	4
CHAPTER 2 LITERATURE REVIEW	6
2.1 Experimental Methodology and Deposition Techniques	10
2.2 Magnetron Sputtering Technique.....	11
2.3 X-ray Powder Diffraction and Characterization Principle.....	13
2.4 UV-Vis-IR Spectrophotometry and Characterization Principle.....	14
2.5 Dektak XT Profilometer.....	17
2.6 X-ray Photoelectron Spectroscopy and Characterization Principle	18
2.7 Hall Effect and Vander Pauw method.....	22
2.7.1 Hall Voltage and Lorentz Force.....	22
2.7.2 Hall Coefficient.....	23
2.7.3 Resistivity	23

2.7.4	Hall Mobility.....	24
2.7.5	Vander Pauw Method	24
2.7.6	Contact Configuration.....	25
2.7.7	Electrical Resistivity Measurement	27
2.7.8	Sheet Resistance.....	27
2.8	Electrochemical Characterization (Basics of electrochemical workstation).....	27
2.8.1	Cyclic Voltammetry	29
2.8.2	Galvanostatic Charge- Discharge	30
2.8.3	Electrochemical Impedance Spectroscopy	31
CHAPTER 3 SYNTHESIS AND STUDY OF CHROMIUM NITRIDE AND CHROMIUM OXYNITRIDE THIN FILMS.....		33
3.1	Experimental Details and Methodology.....	33
3.2	Results and Discussion.....	35
3.2.1	Sample Deposition Rate.....	35
3.2.2	Structural Analysis.....	37
3.2.3	Composition and Topography Analysis.....	40
3.2.4	Elemental Analysis and Cross-Section Characterizations	41
3.2.5	Optoelectronic Study	49
3.2.6	XPS Data Processing, Fitting, Etching, and Depth Profiling Study	56
3.2.7	Hall Effect Analysis and Sheet Resistance Study	67
3.2.8	Electrochemical Behavior Analysis.....	70
CHAPTER 4 CONCLUSION.....		82
REFERENCES		84
VITAE.....		90

LIST OF TABLES

Table 1: Growth parameters of the films	34
Table 2: Film deposition rate and growth time	35
Table 3: Compound's lattice constant and crystallite size	39
Table 4: XPS of Cr 2p peak binding energy, FWHM, area, and % atom of thin films	64
Table 5: XPS of N 1s peak binding energy, FWHM, area, and % atom of thin films.....	64
Table 6: XPS of O 1s peak binding energy, FWHM, area, and % atom of thin films.....	65
Table 7: XPS of C 1s peak binding energy, FWHM, area, and % atom of thin films.....	65
Table 8: Electrical resistivity, Hall coefficient, charge carrier density, mobility, Hall resistance, and types of semiconductors of F1, F2, F3, F4, F6, and F7 thin films on Si(001)	67
Table 9: Electrical resistivity, Hall coefficient, charge carrier density, mobility, Hall resistance, and types of semiconductors of F1, F2, F3, F4, F6, and F7 thin films on fused silica substrates.....	68
Table 10: Hall resistance of the Si(001) substrate of F1, F2, F3, F4, F6, and F7 thin films	68
Table 11: Hall resistance of the fused silica substrate of F1, F2, F, F4, F6, and F7 thin films	69
Table 12: Electrochemical performance of film F1-based symmetric supercapacitor using CV measurement	72
Table 13: Electrochemical performance of film F1-based symmetric supercapacitor using GCD measurement	72

LIST OF FIGURES

Figure 1: Crystal structures of CrN and Cr ₂ N.....	3
Figure 2: Historical flow chart.....	11
Figure 3: Schematic Diagram of Magnetron Sputtering Chamber	12
Figure 4: Schematic of X-ray Diffractometer	13
Figure 5: Schematic of Bragg's Law	14
Figure 6: Schematic diagram of a single beam spectrometer	15
Figure 7: Transmission of light.....	16
Figure 8: Schematic description of the XPS phenomenon of solid surfaces of the related energy concepts	18
Figure 9: Energy diagram of the photoelectron effect.....	20
Figure 10: Van der Pauw Four-probe method	24
Figure 11: Contact Configuration	26
Figure 12: Three electrodes setup	29
Figure 13: Cyclic Voltammetry Circuit Set Up and Cyclic Voltammogram.....	30
Figure 14: GCD graph	31
Figure 15: EIS circuit and Randle equivalent circuit for the electrochemical system.....	32
Figure 16: Schematic fabrication process of film	33
Figure 17: Sample deposition rate on the nitrogen flow.....	Error! Bookmark not defined.
Figure 18: XRD patterns for Si(001) and glass substrate thin films.....	40
Figure 19: SEM pattern of F1, F2 , F3, F3*, F6 and F7	41
Figure 20: EDS of the layered image of sample F1.....	42
Figure 21: EDS of the layered image of sample F3.....	43
Figure 22: EDS of the layered image of sample F7	44
Figure 23: EDS of the layered image of sample F3*	45
Figure 24: Weight percent of map sum spectrum of samples F1, F2, F3, F6, F7, and F3*	46
Figure 25: Cross-section EDS of the layered image of sample F2	47
Figure 26: Cross-section EDS of the layered image of sample F3	48
Figure 27: Cross-section EDS of the layered image of sample F5	49
Figure 28: Tauc plot of CrN/glass of F1, F2, F3, F4, F5, F6, F7 and F3* thin films	51
Figure 29: Energy band gap on the flow rate ratio	52

Figure 30: Extinction coefficient of the thin films.....	53
Figure 31: Film dielectric constants, loss factor, and optical conductivity	54
Figure 32: Film absorbance, absorption coefficient, and nitrogen flow rate influence on the optoelectronic parameters	55
Figure 33: Transmittance and Reflectance	56
Figure 34: Full scan XPS survey of Unetched, etched, and depth profiles of the thin films.....	57
Figure 35: High-resolution XPS spectra of Cr2p of film F1, F2, F4, F5, F6, and F7.....	58
Figure 36: High-resolution XPS spectra of N 1s of film F1, F2, F4, F5, F6, and F7	59
Figure 37: High-resolution XPS spectra of O 1s of film F1, F2, F4, F5, F6, and F7	60
Figure 38: High-resolution XPS spectra of the etched thin films.....	61
Figure 39: High-resolution XPS spectra of the depth profile thin films.....	62
Figure 40: High-resolution XPS spectra of the Cr 2p, N 1s, and O 1s of the unetched, etched, and depth profile of the F4 thin film.....	63
Figure 41: Binding energy of Cr and N depending on the N/Cr ratio	66
Figure 42: Sheet resistance of the thin films.....	70
Figure 43: Comparison of CV curves for the F1, F3*, and F4 electrodes in 3 electrode electrochemical system, using 1 M H ₂ SO ₄ electrolyte	73
Figure 44: CV curves at different scan rates.....	75
Figure 45: GCD profiles at different current densities	76
Figure 46: Areal capacitance from (a) CV and (b) GCD.....	77
Figure 47: GCD profiles at different current densities	78
Figure 48: Nyquist plots of the F6-based symmetric supercapacitor before and after 5000 GCD cycles in the frequency range from 1 Hz to 1 MHz.....	79
Figure 49: Cyclic stability of the F6-based symmetric supercapacitor of capacitance retention (98.2 %) and Coulombic efficiency (97.5 %) up to 5000 GCD cycles at 5 mA/cm ² current density.....	80

LIST OF ABBREVIATIONS

LED :	Light Emitting Diode
PVD :	Physical Vapor Deposition
XRD :	X-ray Diffraction
SEM :	Scanning Electron Microscopy
XPS :	X-ray Photoelectron Spectroscopy
EDS :	X-ray Energy Dispersive spectroscopy
B.E :	Binding Energy
DC :	Direct Current
CV :	Cyclic Voltammetry
GCD :	Galvanostatic Charge-Discharge
EIS :	Electrochemical Impedance Spectroscopy

ABSTRACT

Full name: Waheed Sanjo Kamoru

Thesis title: Growth and Characterization of Chromium Oxynitride Thin Films by RF Magnetron Sputtering for Energy Harvesting and Energy Storage Applications

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This thesis involves the fabrication and characterization of thin films of chromium nitride (CrN) and chromium oxynitride ($\text{CrO}_x\text{N}_{1-x}$) for energy harvesting and energy storage applications. High-quality CrN and $\text{CrO}_x\text{N}_{1-x}$ films were synthesized utilizing radiofrequency magnetron sputtering on Si(001) and glass substrates. During the growth, chromium flux was obtained from a high-purity sputtering target, and nitrogen and oxygen were obtained from a 99.999% pure gas source. The films were grown under different growth conditions and their potential influence on the structure, optoelectronic, and electrochemical properties was characterized by a variety of advanced characterization instruments and techniques such as ellipsometer, UV-VIS-IR spectrophotometer, X-ray diffractometer, scanning electron microscope, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, Vander Pauw four-point probe measurement for measuring electrical resistivity, Hall effect set up, and Vesta. The films were grown with varying nitrogen and oxygen flow rates while keeping the Cr flux constant. The structural analysis by XRD confirms different crystalline compounds such as CrN and Cr_2O_3 . A noticeable change in the crystalline structure, electronic structure, and morphology observed in the film characteristics was due to varying nitrogen and oxygen flow rates. For example, the bandgap of $\text{CrO}_x\text{N}_{1-x}$ has changed in a range from 0.27 eV to 3.56 eV. The Hall coefficient changed from negative to positive values for the CrN films by adjusting the nitrogen flow rate. The films grown with a low nitrogen flow rate showed an n-type semiconducting nature and the films grown with a high nitrogen flow rate demonstrated a p-type semiconductor suggesting that the majority of charge carriers shifted from electrons to holes on Si(001) due to varying nitrogen flow rates. Similarly, the XPS compound spectra of the Cr 2p, N 1s, and O 1s states were scrutinized to establish the chemical or oxidation state information of the surface layer of the film structure according to their binding energy. A

progressive change in the peak intensity and shifting in the three distinctive species observed were ascribed to the effects of the variations of reactive gases (nitrogen and oxygen) flow rates in the films. The electrochemical characterizations of selected films were conducted by the utilization of basic electrochemical workstations such as cyclic voltammetry, galvanostatic charge-discharge or chronopotentiometry, and electrochemical impedance spectroscopy using a 1 mole H_2SO_4 aqueous electrolyte. Our result showed a maximum areal capacitance of 65 mF/cm^2 at a scan rate of 20 mV/sec and 75 mF/cm^2 at 0.5 mA/cm^2 from CV and GCD measurements respectively and similarly with capacitance retention of 98.2% and Coulombic efficiency of 97.5% at 5000 GCD cycle and 5 mA/cm^2 . In conclusion, this work contributes to our understanding of how to optimize the fabrication of CrN , $\text{CrO}_x\text{N}_{1-x}$, and possibly other similar compounds for a wide range of cutting-edge technological applications.

ملخص الرسالة

الاسم الكامل: وحيد سانجو كامورو

للمطببات حصاد RF عنوان الطرحة: نمو وخصائص الغشية الرقيقة من أوكسيدات الكروم باستخدام رش اللمغنون
الطاقة ونظريتها

المختص: فيزياء

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تتضمن هذه الطرحة تصنيع وخصائص الغشية الرقيقة من نيتريد الكروم (CrN) وأوكسيدات الكروم ($\text{CrO}_x\text{N}_{1-x}$) للمطببات حصاد الطاقة ونظريتها. تم تصنيع أفلام CrN و $\text{CrO}_x\text{N}_{1-x}$ على الركائز السيليكون ($\text{Si}(001)$) والزجاج. أثناء النمو، تم الحصول على تدفق الكروم من هدف الخرق عالي النقاء، وتم الحصول على النيتروجين والكسجين من مصدر غاز نيتروجين بنسبة 99.999%. تمت زراعة الأفلام في ظل ظروف نمو مختلفة وتم تحديد تأثيرها المدمج على البنية والخصائص الإلكترونية البصرية والكهروكيميائية من خلال مجموعة متنوعة من أدوات وتقنيات التوصيف المتقدمة مثل قياس القاطع الناقص، وقياس الطيف الضوئي UV-VIS-IR، وقياس حثود الشعاع السينية، ومسح الليزر، مجهر التحليل الطيفي للشعاع السينية المشعة من الطاقة، التحليل الطيفي الإلكتروني الضوئي للشعاع السينية، قياس مسبار ناندر باو رباعي النقاط لقياس المقاومة الكهربية، إعداد تأثير هول، ونظريتها. تمت زراعة الأفلام بمعدلات تدفق مختلفة من النيتروجين والكسجين مع الحفاظ على تدفق الكروم ثابتاً. يؤكد التحليل الهيكلي بواسطة XRD وجود مركبات بلورية مختلفة مثل CrN و Cr_2O_3 كان التغيير الملحوظ في التركيب البلوري والتركيب الإلكتروني والتشكل الذي لوحظ في خصائص الفيلم بسبب اختلاف معدلات تدفق النيتروجين والكسجين. على سبيل المثال، تغيرت فجوة النطاق لـ $\text{CrO}_x\text{N}_{1-x}$ في المدى من 0.27 فولت إلى 3.56 فولت. تم تغيير معامل Hall من القيمة السالبة إلى القيمة الموجبة للأفلام CrN عن طريق ضبط معدل تدفق النيتروجين. أظهرت الأفلام المزروعة بمعدل تدفق منخفض للنيتروجين طبيعة شبه موصلة من النوع n وأظهرت الأفلام المزروعة بمعدل تدفق مرتفع للنيتروجين طبيعة شبه موصلة من النوع p مما يشير إلى أن غلبة حاملات الشحنة تحولت من الإلكترونات إلى الثقوب على $\text{Si}(001)$ وغيروا ذلك لمعدلات تدفق النيتروجين المختلفة. وبالمثل، تم فحص أطراف مركب XPS لحالات $\text{Cr } 2p$ و $\text{N } 1s$ و $\text{O } 1s$ لتحديد معلومات الحالة الأكسيماية أو حالة الأكسدة للطبقة السطحية من بنية الفيلم ونظراً لطاقة الترابط الخاصة بها. كما يُعزى التغيير التدريجي في شدة الذروة وال تحول في النواحي المموجة التي تمت ملحظتها إلى تأثيرات التغييرات في معدلات تدفق الغازات المتفاعلة (النيتروجين والكسجين) في الأفلام. تم إجراء التوصيف الكهروكيميائي للأفلام المخزونة من خلال استخدام محطات العمل الكهروكيميائية الأساسية مثل قياس الجهد الدوري، أو تدرج الشحنة الجلفانية أو قياس الجهد الزمني، والتحليل الطيفي للمقاومة الكهروكيميائية باستخدام 1 مول من الليتروليت المائي H_2SO_4 . أظهرت نتائجنا سرعة مساحة قصوى تبلغ 65 مللي فاراد/سم² بمعدل مسح قدره 20 مللي فولت/ثانية و 75 مللي فاراد/سم² عند 0.5 مللي أمبير/سم² من قياسات CV و GCD على التوالي، وبالمثل مع الحفاظ بالسرعة بنسبة 98.2% وكفاءة كوانتوم تبلغ 97.5% عند دورة GCD 5000 و 5 مللي أمبير/سم². في الختام، يساهم هذا العمل في فهمنا لخصائص التحسين في صناعة ونظريتها CrN ، و $\text{CrO}_x\text{N}_{1-x}$ ، وربما مركبات أخرى مماثلة لمجموعة واسعة من التطبيقات الإلكترونية الواعدة.

CHAPTER 1

INTRODUCTION

1.1 Transition Metal Nitride

Energy demand is growing rapidly due to population growth, global warming, economic expansion, and technological innovation. To meet this demand, scientists are investigating new materials to explore different energy sources and store the harvested energy more efficiently. This innovative technological energy demand that offers a sustainable and eco-friendly solution to satisfy end-user needs is firmly entrenched. The non-conventional energy sources (Renewable energy sources) such as solar and wind energy because of their relative abundance for many years have been evident to have contributed to green energy power generation. Several energy-harvesting materials such as solar cells, silicon, organic or inorganic semiconductors, and thin films have been depicted to enhance the harvesting application of the energy. Thereby, an increase in the demand for these energy products has called for an interest in the investigation of solar harvesting materials and electrochemical energy storage devices, particularly in examining the performance of the electrode material which plays a greater role in the energy storage mechanism. Significant progress has been achieved in employing metal oxides, polymers, transition metal nitride, and carbon-based materials as potential electrode materials.

Transition Metal Nitrides (TMNs) have tremendous qualities such as mechanical strength, hardness, high corrosion, outstanding electrical and thermal resilience, magnetic properties, and spintronics, and are used as working electrodes in supercapacitors. These metals demonstrated a high conductivity, excellent electro-catalytic activity, and energy density that make them appropriate electrodes for energy storage devices. Some transition metals performance could be enhanced by forming ternary, quaternary, and multicomponent thin films.

TMNs have interfacial and adsorption characteristics that are comparable to those of the platinum group metals [1,2]. The study established that conventional nitrides of transition metal can exist in three different crystallographic forms: face-centered cubic (FCC), hexagon-closed packed (HCP), and simple hexagonal structures (HEX) [3]. A family of commonly researched transition

metal nitrides, in which nitrogen-rich atoms fill the interstitial positions of the parent metal lattice, includes vanadium nitride (VN) [4,5], titanium nitride (TiN) [6,7], chromium nitride (CrN) [8,9], tantalum nitride (TaN), zirconium nitride (ZrN), TiN/ZrN [10], and niobium nitride (NbN).

1.2 Chromium Nitride

Chromium Nitride has garnered significant scientific interest [11–13] aside from the general properties of transition metals properties mentioned above, owing to their electronic, optical, and magnetic properties. It has high corrosion resistance, and chemical stability and is ideal for operating in harsh conditions such as high or low temperatures. It is a model system that interplays between structural, electronic, and magnetism. It demonstrates a first-order magneto-structural change from a room temperature paramagnetic cubic (Fm-3m) phase to a low temperature antiferromagnetic, orthorhombic state below its Neel temperature of 280 K, and shows semiconducting properties at room temperature, whereas metallic properties at low temperatures.

It is a major contender for miniature electronic systems [14], particularly during heating processing, oxidation processing, low thermal conductivity, and corrosion-resistance properties. Another field of study of CrN that has made significant strides in the past few years is its use in supercapacitor applications. Chromium nitrides are excellent candidates for use as supercapacitor working electrode materials because of their extremely specific capacitance and charge cycle retention [15–18].

Chromium nitride is a cubic fcc rock salt interstitial compound vulnerable to stoichiometry structure deficiency because of the occupancy of the nitrogen-containing atoms of the octahedral spacing between the chromium atoms in the lattice. chromium nitride exhibits covalent bonding between chromium and nitrogen atoms, and it has emerged as a potential material for energy harvesting due to its crystallographic, electronic, and chemical stability properties. The semiconductor properties and thermoelectric application of CrN is due to its varied crystallite orientations, good oxidation resistance, and low coefficient of thermal expansion. The preferred plane orientations such as (002), (111), and (022), structural, and thermal conductivity enhancing the performances of CrN is a distinctive characteristic that extensively shows the applications of CrN thin films.

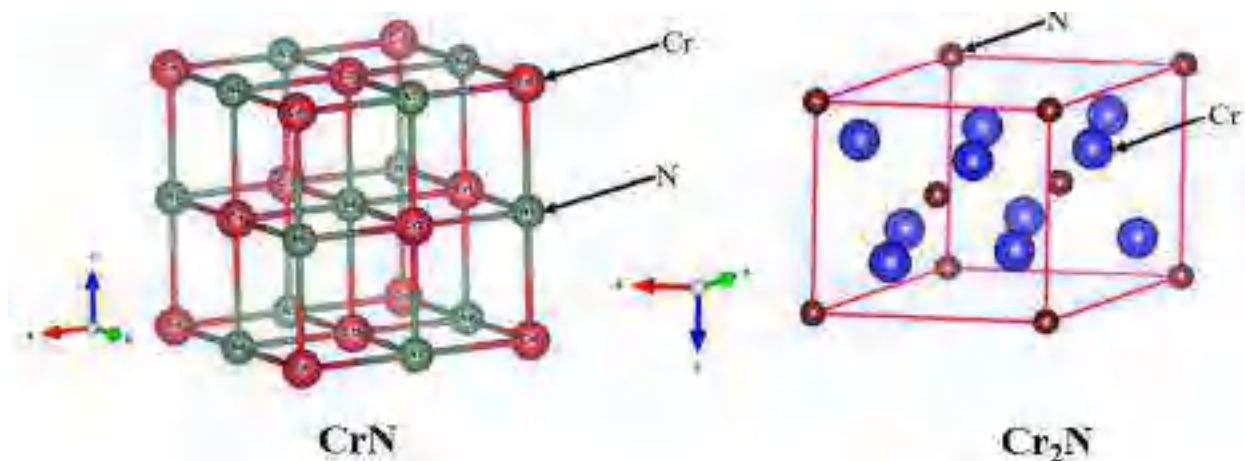


Figure 1: Crystal structures of CrN and Cr₂N

In Cr-rich films, hexagonal Cr₂N can form which is a second phase of a CrN film, which is also an interstitial molecule [19,20]. Cr₂N exhibits a more covalent bonding than the cubic phase CrN and this substantial covalency is attributed to higher hardness than the fcc phase of CrN.

1.3 Chromium Oxide and Oxynitride

Transition metal oxynitrides possess countless applications in technology due to the fact of difference between metal oxides and nitrides with respect to their range of properties. As a result of this, the compound gained the combinations of hardness and toughness from oxides and nitrides respectively. The electrical, optical, and mechanical properties can be adjusted mainly for the energy gap and crystals order of the oxides and nitrides by balancing the ratio of oxide to nitride in the composition of the films such as TiO_xN_y, ZrO_xN_y, TaO_xN_y [21–27]

Chromium oxynitride films possessed features of chromium oxide film and chromium nitride film, which could be fabricated by the addition of a small quantity of nitrogen gas to an existing chromium oxide film or by the addition of quantifiable oxygen gas to an existing chromium nitride film. Chromium oxynitride films have been used extensively in optics, wear, corrosion, and electrical and chemical stability qualities owing to their potential in the modification of the nitrogen-to-oxygen flow rate ratio [28,29]. Typically, chromium oxynitride compound is thought of being a physically combined compound of chromium nitride (CrN) and chromium oxide (CrO_x) instead of being a singular phase chromium oxynitride [30]. Hence, it contained toughness and hardness from both CrN and CrO_x respectively. Depending on its stoichiometry, CrN exhibits narrow bandgap semiconducting properties, whereas CrO_x is a wide bandgap semiconductor at

room temperature. Because they differ from metal oxides and nitrides in terms of their variety of characteristics, transition metal oxynitrides have endless possibilities in technology.

This compound, because of its fascinating properties such as good mechanical strength, physical shin appearance, and chemical composition, has been highlighted for various industrial applications. A few examples of its technical applications in solar absorbers, working electrodes for electrochromic windows, and protective coating [31].

Chromium oxide (Cr_2O_3) is the most thermal resilient compound in a surrounding atmosphere [32] and can be grown using various physical and chemical vapor deposition methods. Therefore, chromium oxides come in a wide range of forms with different structures and chemical states. These forms may be the primary cause of the wide range of properties observed under growth conditions at low temperatures and pressure. Below Neel temperature, Cr_2O_3 exhibits unique physical features that make it a promising material for spintronics applications.

1.4 Thesis Objective

This research goal is to study the fundamental properties of chromium nitride and chromium oxynitride thin films fabricated on silicon and glass substrate by RF magnetron sputtering and study them for applications such as solar energy harvesting, ultraviolet radiation protection, and supercapacitor working electrodes. The films were synthesized by radiofrequency sputtering technique, where high-purity chromium (Cr) was installed as the potential target substrate, and reactive gases (nitrogen, oxygen), and processing gas (argon) were supplied to the growth chamber to influence the property of the film. The effects of varying the growth parameters on the structural, optoelectronic, and electrochemical performances of the films were assessed by UV-VIS-IR spectrophotometer, X-ray diffractometer, scanning electron microscope, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, Van der Pauw probe measurement of the electrical resistivity, and Hall effect set up. The XRD data was also theoretically modeled using Vesta and detailed structural information was obtained. The procedures to achieve this include:

1. Thin film fabrication and growth on silicon and silica substance by using an RF magnetron sputtering system with varied processing gas and reactive gases flow rates.
2. Optical characteristics study of the grown films by using UV-Vis-IR spectrophotometry.
3. Examination of the structure of the thin films by X-ray diffraction.

4. Investigation of the surface profilometry by Dektak XT profilometer.
5. Study the texture and topography by using scanning electron microscopy.
6. Chemical or oxidation state information of the surface layer of the film structure investigation by using an X-ray photoelectron spectroscopy.
7. Hall Effects characterization examination of electron properties with a key objective on the study of the carrier concentration, semiconductor type, and Hall mobility of the grown thin films.
8. Electrochemical characterizations using cyclic voltammetry, galvanostatic charge-discharge (chronopotentiometry) measurements, and electrochemical impedance spectroscopy.

CHAPTER 2

LITERATURE REVIEW

The fundamental properties and applications of CrN and $\text{CrO}_x\text{N}_{1-x}$ thin films reported in the literature are making interesting materials for studying them for fundamental science as well as for advanced technological applications owing to their tunable properties. The fundamental properties of these thin films are reported to be extremely sensitive to the growth conditions and their stoichiometry. In this chapter, literature is carefully surveyed, which puts the current project into perspective.

Various thin film growth techniques can be used to deposit CrN thin films on different substrates with precisely regulated compositions. Among the techniques used for the deposition of CrN are DC magnetron sputtering [33], radio-frequency sputtering [34–36], DC reactive magnetron sputtering [37,38], molecular beam epitaxy [39–41], and so on have been used. By regulating processing variables such as chamber pressure during the growth, pumping speed, reactive gas flow rate, sputtering power, substrate rotation, and substrate heating the sputtering process can be efficiently controlled. The sputtering process is cost-effective, provides good control over the growth parameters and stoichiometry of the deposited films, and is ideal for industrial-scale production.

Alam et al. [42] have investigated a CrN thin film properties synthesized by reactive radio frequency magnetron sputtering techniques on silicon and glass material using argon and nitrogen as processing and reactive gases, respectively. Their study focused on the potential impact of varying the nitrogen-to-argon ratio flow rates on the film's bandgap, structure defect, and electron phase transition. Two growth orientations [111] and [002] of CrN were reported while the band gap, thickness, and crystallinity changed due to the nitrogen to argon flow rates. They observed discontinuity in the resistivity vs temperature data due to an electronic transition from semiconducting to either metallic or insulating state depending on the film stoichiometric ratio.

Corliss et al. [43] have investigated different compounds having predominantly ionic characteristics using neutron diffraction. They examined the CrN compound and found it to be a nonionic interstitial molecule, crystallized with a rock salt structure. They found it in an

antiferromagnetic phase at low temperatures with the Neel point of 0°C. The neutron diffraction experiment revealed that the fourth sort of magnetic arrangement has moments arrayed in double ferromagnetic sheets that alternate simultaneously to a plane parallel to a face-diagonal. Below the transition, the structure is orthorhombic, and the space group was provisionally designated. The diffraction data have allowed for a partial determination of the atomic displacements associated with the distortion, which are described in connection to the magnetic structure orientation.

In 2017, the crystalline structure and electrical properties of CrN thin films prepared on Si(100) material up to a few hundred nanometers thickness were studied by Akkera et al. [44]. Their films were fabricated by a DC reactive magnetron sputtering with pure chromium (Cr) metal as the targeting material. The crystal structure of the sputtered CrN/Si (100) films was reported to change from the hexagonal phase (β -Cr₂N) to the cubic phase (CrN) due to an increase in the thickness of the films. Structural phase transition of hexagonal phase (β -Cr₂N) (002) and cubic phase (CrN) (111) were also seen to have crystal orientations of (200) and (311). The transformation in the structural transition is explained by a reduction in the film-substrate interfacial strain. The electrical resistivity measurements showed that CrN grown on Si(100) films with a 150nm thickness only showed semiconducting behavior at 250 K temperature range whereas films with a lower and higher thickness than the latter underwent a semiconducting characteristic for the whole temperature range.

The influence of deposition rates in the sputtering system on the controllability of the morphology of CrN-grown films was investigated by Nam et al. [45]. They asserted that the production of the CrN compound rather than pure Cr was mainly caused by ionization efficiency brought about by the pulsed DC bias. Research on the effects of deposition variables and stress on the strength and microstructural characteristics of CrN films grown on a substrate by magnetron system showed that the films exhibit a changing density influenced by coating.

Jayatissa et.al [45] have studied the characteristics of CrN films grown on three different samples by using a radiofrequency magnetron sputtering method. The study focused on varying three growth conditions namely, temperature, chamber partial pressure, and power were reported to pose an influence on the microhardness, and optical properties by using a Cr target. The roughness, hardness, and adherence were assessed by corrosion examination before it was used as a coating material. They gathered that altering the substrate temperature, nitrogen flow rates, and power

during sputtering deposition had an impact on the CrN films. Important features of the developed CrN were stated to include electrical conductivity, optical attributes, toughness, and substrate adhesion.

Shah et al. [46] studied the effects of sputtering variables such as temperature, pressure, and radiofrequency potential on the microscopic structure characteristics of CrN steel-coated thin films using argon as a processing gas and nitrogen as a reactive gas while other chamber parameters were kept constant. The XRD analysis revealed that CrN films have crystallized in several phases and textures. The films were grown predominantly in the plane (111), but values of intensity reduced when compared to the peak plane (200) as the chamber pressure increased during the growth. The chamber pressure and the power sputtering influence effect demonstrated that the films deposited at lower radiofrequency powers experienced greater pressure-related stress than films grown at high radiofrequency power. Based on the report, they found that the ideal phase orientation of grown CrN films is affected by the number of atoms sputtered per unit growth time that influenced the mean free path of the ejected atom and the collision of the sputtered particle.

In addition to their exceptional specific capacitance, outstanding chemical stability, good electrical conduction properties, and excellent cycling stability, transition metal nitrides have recently demonstrated significant promise as supercapacitor working electrode materials [47,48]. Most of the published work is focused on the study of TiN [49,50], VN [51], and Mo₂N [52] while reports about the study of CrN [18,19] for the supercapacitor working electrodes are rare.

Arif et al. [18] studied the capacitive performance of a CrN thin film working electrodes sputtered on steel to investigate the specific capacitive behavior of the film working electrodes through the examination of two different electrochemical characterization techniques. The curves of the cyclic voltammetry measurement at rapid scan rates for the CrN thin films and steel current collectors were obtained. They discovered that film is the crucial component of the capacitive potential of the electrodes. They achieved a consistent specific capacitance of 41.6 F/g at 5 mV/s and good retention with excellent durability up a long cycle number.

Wei et al. [17] symmetric supercapacitor CrN films growth study utilizing a DC magnetron sputtering. The prepared films were grown at an adequate potential with an applied power of 250 W and vacuum maintained at low pressure and oxygen and nitrogen were used as the processing

and reactive gases respectively. Electrochemical characterizations were performed to investigate the CrN thin films working electrode potential. The CrN films employed as the working electrodes exhibited good cycling stability and excellent retention after certain cycles in a half-value mole of acidic H_2SO_4 electrolyte. The symmetric supercapacitor has exceptional cycling stability and a high energy density at a low power density. Structural and compositional characterizations were carried out to establish the surface properties of the grown films.

To increase the stability of perovskite-based photovoltaic cells, Zheng et al.[53] studied the chromium oxides as an electron-transporting material medium. In the study, two deposition techniques were used for the growth of chromium oxynitride ($\text{CrN}_x\text{O}_{1-x}$) thin films. They reported a solution of different halide perovskite by focusing on the inverted perovskite solar cell device to enhance its stability. They found that the addition of the CrOX interfacial layer enhances stability, improves power conversion efficiency by 17.5%, resists water and oxygen on the active layer, and prevents the metal electrodes and perovskite layer reaction.

Julkarnain et al. [54] reported the properties of thermally evaporated Cr_2O_3 grown films on glass substrate at ambient temperature and low base pressure. The oxidation of Cr to Cr_2O_3 is undertaken in a vacuum coating by evaporation. The sample is further annealed at higher temperatures of 570 K for certain hours for stability improvement of the films. Notable surface characterizations were used for the determination of the potential influence. The SEM analyses of the samples showed a uniform growth overlapping the entire surface which induced that the film growth is not stoichiometric inclined. The notable integral optical parameter obtained suggests the material for application in surface devices.

According to Wierzchon et al. [55], comparing CrN to $\text{CrN}_x\text{O}_{1-x}$ films, it was claimed that $\text{CrN}_x\text{O}_{1-x}$ films exhibit greater corrosion resistance, better adherence, and structural uniformity. They reported that the fabricated CrN thin film surface layers formed depend on the processing temperature. They discovered that as the temperature drops, the resistance of the film towards corrosion rises because their susceptibility to corrosion shifts from negative to positive, while other passive state parameters fall.

The hardness of chromium oxynitride Cr(N, O) film fabricated by using a pulsed laser technique was characterized in the study by [73]. The film was grown by setting the reactive gas oxygen

flow rate as the controllable gas. In his findings, they asserted that the Cr(N, O) constitutes chromium, oxygen, and nitrogen and by modifying the oxygen partial pressure in the film, the chromium content of the film was found to be closer to the Cr_2O_3 at higher oxygen levels.

Rawal et al. [28] have investigated the optical characteristics and energy difference of chromium oxynitride films. They described how the hydrophobicity, optical properties, and structure of $\text{CrN}_x\text{O}_{x-1}$ films grown on a substrate were affected by the inert gases. They discovered that using helium gas as the processing gas prepared a rougher surface than argon gas, with also a higher angle of contact and lower energy at the surface. The increase in the bandgap using the two processing gases is attributed to an increment in the oxygen partial pressure. It was affirmed in the report that the films were potentially effective for protective coating application for water repellent.

2.1 Experimental Methodology and Deposition Techniques

The utilization of thin film features, such as thermal resilience, adhesion, porosity, and suitable stoichiometry, among others, is the foundation for contemporary technologies. These properties are actively researched and have grown to be one of the most significant industrial concerns. Zirconium, tantalum, chromium, and titanium have been among the transition metals used often as the target materials in the deposition of thin films on a substrate by various convention methods due to their excellent exhibit behavior under severe conditions [56,57]. The development of various deposition methods and the control of operating parameters have made it attainable to achieve protective coatings with excellent wear resistance, exceptionally high toughness, as well as heat and chemical resilience. The common deposition techniques used have been chemical vapor deposition (CVD), and physical vapor deposition (PVD). PVD is widely applied to grow films with thicknesses as low as a few nanometers. Diode sputtering, DC and RF magnetron sputtering, and ion-beam sputtering are some examples of PVD technologies [58].

The sputtering technique is one of the kinds of physical vapor deposition techniques. The physical vapor technique includes several forms such as magnetron sputtering, ion-beam sputtering, gas flow sputtering, and ion-assisted sputtering among others. The technique has been put into practice in the optical coating industry and magnetic storage disk applications since the 1800s in the report by Green, J.E [78]. The improvement to the device is recorded to have been happening after its inception. For example, the development in the later year resulted in radiofrequency glow

discharge. Rapid advancement followed in 1921 leading to the magnetron system. By the late 1930s, reports of experiments done by using the magnetron-sputtering system had already been available to official open access. The conception and initiation of capacitated connected radiofrequency puttering devices started in the early 1960s. The next year, 1962, the introduction of the parallel-plate magnetron commenced. A progressive advancement to the technique continued year after year and notably in 1975 (direct current pulsed and mid-frequency AC sputtering), tiltable sputtering in 1980. During the 1990s, two new forms of magnetron sputtering emerged, both aiming to produce metal atoms that were sputter-ejected with ionization efficiency. In 1992, the idea of tunable imbalance magnetron sputtering was developed. The sputtering deposition flow chart from history is shown below.

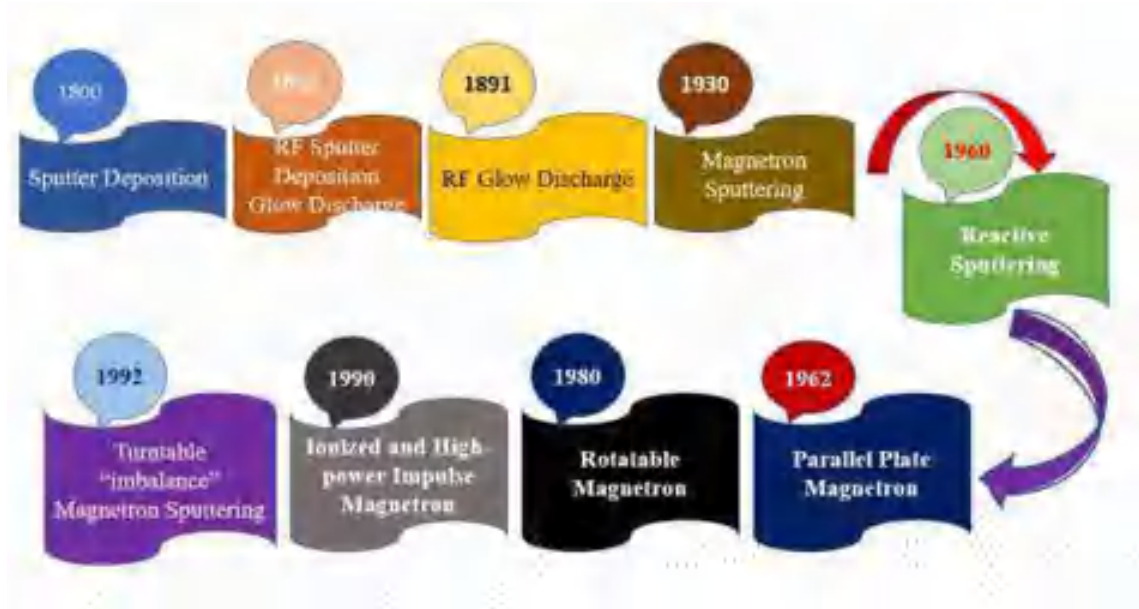


Figure 2: Historical flow chart

2.2 Magnetron Sputtering Technique

Magnetron sputtering has advanced quickly over the past few decades among PVD thin film fabrication techniques. In coatings, it is the most popular technique for depositing transition metals, alloys, metal oxides, carbides, and nitrides on a various substance, including metals, metal alloys, fused silica, porcelain, ceramics, and polymers [59–61]. The processing takes place in a reaction chamber which comprises two electrodes connected within. The target material or sample is positioned on the surface of the negatively charged electrode while the substrate is centered and

the positively charged electrode, or a grounded electrode, and the electrodes are connected to the direct current or a radiofrequency source.

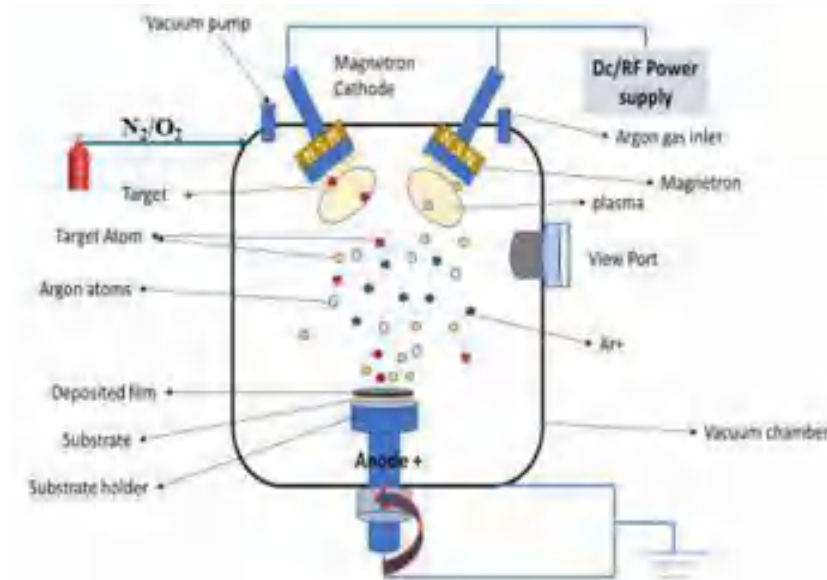


Figure 3: Schematic Diagram of Magnetron Sputtering Chamber

The growth chamber is pumped out to a low pressure of a smaller Torr to remove contaminants and guarantee a high level of pure film. The procedure is initiated by bombarding the target material with positive ions, usually from a noble gas such as argon to the chamber through the inlet. The stray electron collides with the uncharged gas atom and converts it to a positively charged ion. The positively charged ion traveled toward the cathode owing to the difference in polarity between the cathode which is negatively charged and the ionized gas which is positively charged and then bombarded the surface of the target material. These ionized gases bombardment on the surface of the target positioned at the cathode with high energy sufficient to sputter atoms finally sputtered off atoms from the target and then, the removed atoms decelerate downward to the substrate which is assisted by the applicable vacuum that provides an adequate enabling free mean path for sputtered atoms to deposit on the substrate surface. The bombarding ionized gas at the target surface could result in other ion interactions aside from sputtering due to processing parameters such as reflection, adsorption, sputtering, electron and photon emission, and other ion interactions. In such a situation, the growth conditions are optimized to favor sputtering. Other parameters such as applied power, chamber pressure, collision energy, and the applied potential should be considered.

2.3 X-ray Powder Diffraction and Characterization Principle

X-ray diffraction (XRD) is a remarkably adaptable analytic approach that provides qualitative detail about the phase orientation and crystallinity of a material. XRD is incredibly helpful for grain size analysis and stress measurements. In 1912, Max Von Laue discovered a crystalline material with similar behavior toward X-ray wavelengths like three-dimensional diffraction gratings due to the spacing planes in the crystals. Nowadays, it is a common tool to examine crystallization forms and atomic spacing. The phase of a material can be determined by comparing diffraction patterns from unidentified samples to patterns from reference database libraries. The International Center of Diffraction Data (ICDD) is a collection of X-ray patterns published in the scientific literature; the X-ray patterns obtained from samples are then compared with the ICDD reference database to determine whether the known or unknown phases exist in the sample.

An extensive range of materials, including metals, liquids substances, minerals, pharmaceuticals investigation, photovoltaic cells, plastics, polymers compounds, semiconductors technologies, and thin-film coatings, can be analyzed using high-tech, non-destructive X-ray diffraction techniques. The presence of flaws in a certain crystal, degree of stress resistance, degree and size of crystallinity, texture, and essentially every other element pertinent to the fundamental structure of the sample may all be easily determined by XRD analysis [62].

The constructive interference of an X-ray source of a single wavelength with the crystalline material produces an X-ray diffraction. The rays are produced in a cathode ray tube which is then filtered and collimated for optimization.

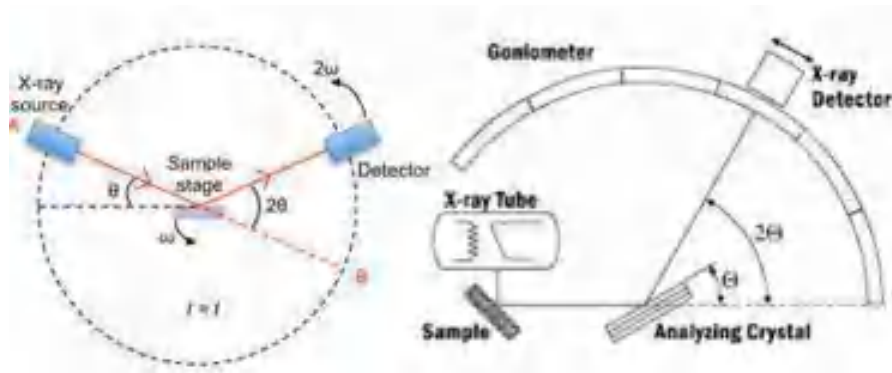


Figure 4: Schematic of X-ray Diffractometer [62]

The X-ray beams are passed through the samples for analysis. The X-rays then move through the sample, extruding out an atom in the structure to change the beam path and angle relative to the original beam. The diffraction angle obtained is used to calculate the difference between atomic planes.

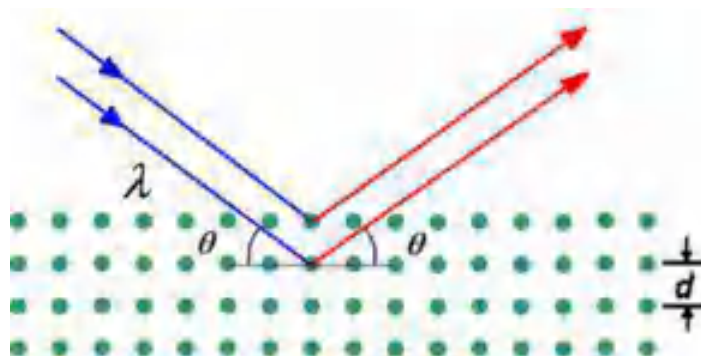


Figure 5: Schematic of Bragg's Law

The constructive interference of the diffracted ray by the incidence of the primary rays with the atoms occurs when Bragg's law is satisfied:

$$2 d \sin \theta = n\lambda$$

where d , θ , n , λ are the interplanar spacing, diffraction angles, order of maxima, and the wavelength of the X-ray respectively. The law affirmed a relationship between the spacing, diffraction angle in the crystal structure, and the wavelength of the incident radiation. Once the sample has been scanned over a range of 2 theta angles, different lattice diffraction orientations are obtained. The diffracted radiographs are identified, noted, and compared to the database. Since each compound has a unique collection of interplanar spacings (also called d-spacings), it is possible to define the compound by relating the diffraction peaks with the interplanar d-spacings. The typical method for doing this is by comparing the d-spacings with standard reference pattern

2.4 UV-Vis-IR Spectrophotometry and Characterization Principle

Ultraviolet-visible-infrared spectrophotometry is an instrument that makes use of the utilization of a light source to irradiate a sample with light spanning to some certain range of wavelengths of the electromagnetic spectrum such as (ultraviolet to visible to infrared wavelength range). Many different processes, including absorption, scattering, reflection, fluorescence, phosphorescence, and photochemical reactions are possible to occur when light interacts with materials. The spectrophotometry technique is used to determine the wavelength dependency on light intensity.

The key component of the instrument is to measure the wavelength of the diffracting beam, the intensities using a charge-coupled device, and subsequent graphing of the effects on the computer. A radiating light source such as tungsten filament or its similar source, a holder, a wavelength separator diffraction grating and a slit, the rotating disks, sample and reference cells, detector, and computer. There are two types of spectrophotometers depending on the number of beam(s) used in the system: single beam and double beam. The difference between these types involves the intensity set to radiate the sample. In single-beam instrumentation, the initial intensity I_0 is measured by removing the sample from the instrument and a single light completely passed through the sample cell while in double-beam instrumentation, before reaching the sample, the light is separated into two beams in which one beam is utilized as the reference and the other to irradiate the sample.

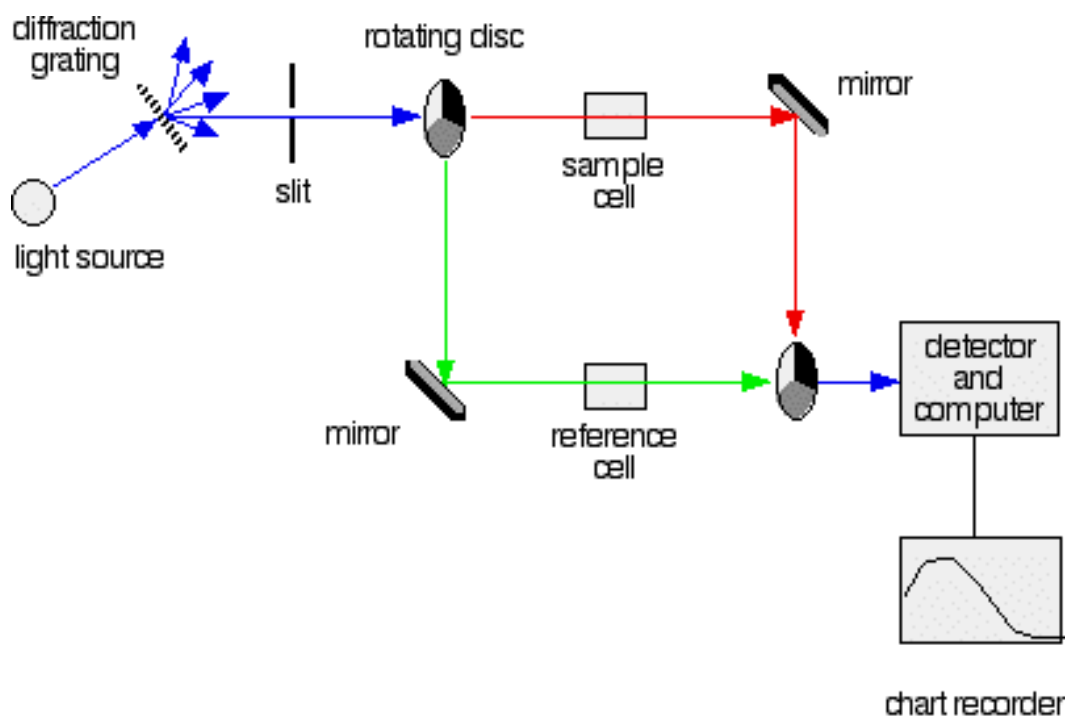


Figure 6: Schematic diagram of a single beam spectrometer [63]

The instrument working principle involves the measurement and comparison of the light intensity before and after passing through a sample. The absorbance and the reflectance are related in terms

of the incident (I_0) and transmitted light (I). According to Beer-Lambert Law, the ratio of the intensity of the incident light (I_0) to the intensity of the transmitted light (I) is related as:

$$I = I_0 e^{-\alpha x}$$

where α is the absorbance and x is the thickness. Re-arranging and taking the logarithm of both sides:

$$\log\left(\frac{I}{I_0}\right) = -\alpha x \log(e)$$

$$\log\left(\frac{I_0}{I}\right) = 0.4343\alpha x$$

The absorbance (A) is defined as $A = \log\left(\frac{I_0}{I}\right)$. Therefore, the absorbance coefficient α is expressed as:

$$\alpha = 2.302 \frac{A}{x}$$

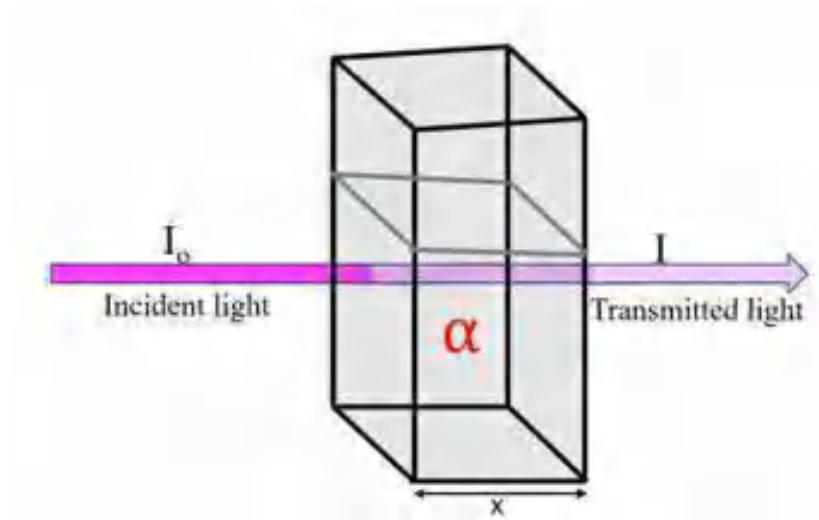


Figure 7: Transmission of light

The workings ideal of optoelectronic appliances are based on the combined concepts of optics and electronics that depend on the quantum mechanics effect of photons on electronic materials to transform light into electrical signals and the other way around. Both the efficiency and precision

of these devices are greatly influenced by the electronic characteristics of the responding material. Solar cells, photodiodes, organic field effect transistors, laser diodes, emitters, and detectors for telecommunications and automated technology are just a few of the optoelectronic applications. The basic features of these devices depend on the semiconductors, and the dopants activeness rather than the separation of an electron to the hole, the excitation and recombination occurrence to realize an extremely efficient emission or photon detection [64–67]. Fabrication of optoelectronic devices features such as energy bandgap, absorption, and extinction coefficients, refractive index, and dielectric coefficient are highly important optical characteristics for their design [68,69]. The refractive index of the semiconducting devices enables the easy path for the numerical analysis of the constructed devices especially in LED for the proper simulation of the angular dependency of light transmission and extraction. It also plays a significant impact determining the anti-reflection effectiveness of the material, exterior, and inner performance of LED polymers [58,70,71].

2.5 Dektak XT Profilometer

The Dektak XT is a surface profile-measuring device that uses a mean diamond tip with a stylus to touch the sample. The sample stage slides the sample according to the stylus tip to create a profile, and the tool retains a consistent stylus force throughout. The device measures the lateral dimensions of sample structures and step heights by profiling the surface topography. Other measurements that could be performed by the instrument include roughness determination (above ~ 15 Å range), stress analysis, and mapping capabilities. The tool is capable of measuring profile step heights of ~ 500 Å to 100 μm , and a step-small height accuracy which is affected by noise floor or surface roughness.

2.6 X-ray Photoelectron Spectroscopy and Characterization Principle

X-ray photoelectron spectroscopy (XPS) is a surface analytic, non-destructive spectroscopic technique working on the principle of photoelectron electron emission. It is frequently utilized to evaluate the surface elemental identification or constituents of a material, the abundance of the surface elements, its chemical states (oxidation state), electronic state and species, the density owing to their binding energy of the elements found, as well as film thickness. Various material surfaces, including inorganic compounds, semiconductor devices, organic chemical substances, films, and so on can be characterized using XPS. The surface bombardment of X-ray photons in XPS is used to back research on surface-mediated processes in redox, evaporation or deposition, catalysis, and absorption reactions. The vacancy created by the X-ray with energy at the electron core level and the binding energy.

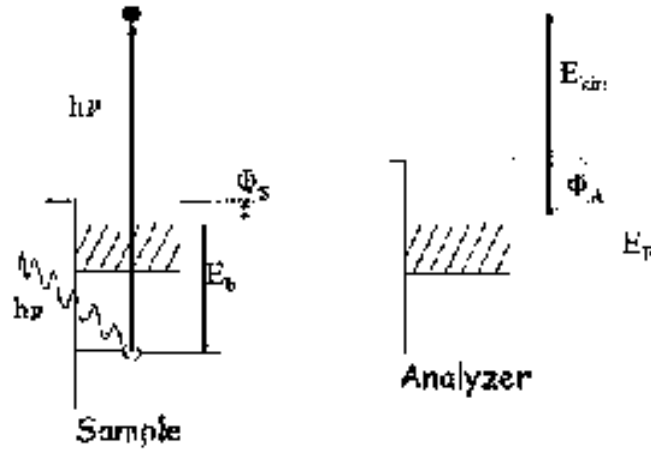


Figure 8: Schematic description of the XPS phenomenon of solid surfaces of the related energy concepts [72]

$$E_{kin} = h\nu - E_B - \phi_S - (\phi_A - \phi_S)$$

$$E_{kin} = h\nu - E_B - \phi_A$$

The constants ϕ_A is the Analyzer's work function, $h\nu$ is the x-ray energy from the source, due to their comparatively high energy and narrow width, E_{kin} and E_B are the released electron kinetic energy and binding energy.

The elucidation of an XPS is due to the photoelectric effect mechanism firstly categorized by Einstein in 1905, and from here, it has an extended heritage that can be traced to recent studies in

which the photoelectrons are ejected by the excitation of the gamma-ray or an X-rays. Since the late 1950s, the photoelectric effect has developed into one of our most reliable techniques for determining the electronic structure and chemical form of matter. In 1981, Kai Siegbahn received the Nobel Prize for his work in XPS device fabrication [72]. When combined with ion-beam etching, the method can be utilized for depth profiling. It is often used to study material chemical compositions before or after exposure to a physical phenomenon.

(a) X-ray Photoelectron Spectroscopy Fundamental Principle

The foundation of the XPS device working technology is based on photoemissions of an electron of an incident photon on a material in an ultrahigh vacuum environment (UHV) when exposed to a very powerful monochromatic X-ray source (tungsten, or LaB₆) filament, which causes the electrons in the sample core levels to absorb the energy of the photons and release them with kinetic energy. The kinetic energy and the number of the emitted electrons are simultaneously recorded by detectors [73]. The electron binding energy is determined by the difference between the photon energy and the combination of the kinetic energy of the electron instrumental factor termed the work function. The work function is frequently seen as a varying instrumental modification factor because it varies on both the detector and the substance. An analysis of the measured number of photoelectrons detected as a function of binding energy yields the XPS spectrum. The fundamental oxidizing state, and the regional bonded surroundings, such as the nature of the nearest neighbors, bonding polymorphism to the nearest neighbors, and so on, all have an impact on the B.E of the electrons, which is a property of the constituent elements. An assortment of distinctive XPS peaks is produced by each constituent. The electron configurations of the electrons in the atom orbitals such as 1s, 2s, 2p, and 3s, are represented by these peaks. The peak electron count corresponds to the amount of each element present in the XPS sampling volume.

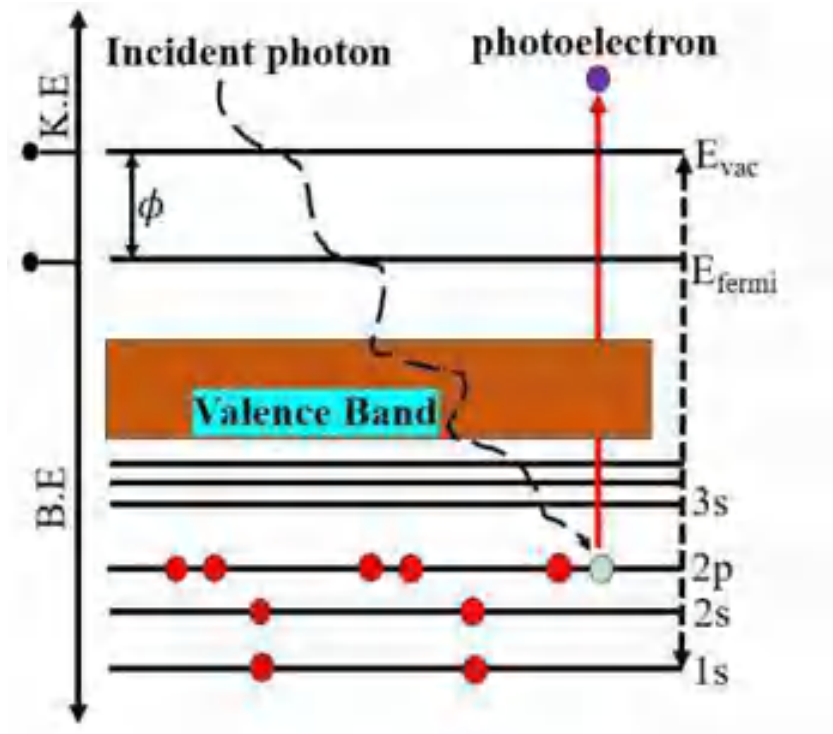


Figure 9: Energy diagram of the photoelectron effect

since the energy of the incident photon and kinetic energy of the ejected electron are known, the binding energy of the electron can be determined by the following equation: The binding energy is obtained from the equation below:

$$E_{kin} = E_{photon} - (E_{B.E} + \phi)$$

where E_{kin} is the kinetic energy of the photoelectron, E_{photon} is the energy of the incident photon, $E_{B.E}$ is the binding energy of a given electron. and ϕ is the work function, the energy difference between the vacuum and Fermi energy level. Because the work function for a specific XPS configuration is constant and serves as a reference point, the $E_{B.E}$ maybe determined by using an analyzer to measure E_{kin} using the above equation. Understanding the kinetic energy of an ejected core electron can reveal a great deal about the substance [74].

(b) Depth Profiling

XPS depth profiling measurement enables the characterization of chemical composition in relation to the depth of the sample. The technique is accomplished by combining a series of interspersed ion gun etch cycles with the present XPS result. It is achieved by tilting the outer surface of the sample to about 10-20 nm thickness for quantitative information examination to reveal subsurface details of different materials. The depth profile of an XPS measurement relates the intensity of the photoelectrons at the surface and the intensity of the photoelectrons at a depth below the surface. According to Beer-Lambert law, the intensity at the surface to the intensity below the surface is given as:

$$I_s = I_o e^{-d/\lambda}$$

where d is the depth below the surface. The depth profile is achieved when XPS measurements are combined with an ion beam gun. The material is etched using an ion gun for a while, and then the ion gun is turned off to collect XPS spectra. With each ion gun cycle exposing a new surface, the structure of those surfaces may be determined by studying the resulting XPS spectra.

(c) Chemical State and Chemical Shift

The chemical state feature of an XPS is obtained from the atomic species in locally bonded environments of a few surface nanometers. The oxidation state, closest neighboring atoms, and bonding affinity to those nearest or next-nearest neighbors all have an impact on the local bonding environment. The normal peak of carbon binding energy of the sample could shift from 284.6 eV to values below or above it. The modification of the atom state or chemical environment upsets its energy level and hence results in a subsequent variation of the binding energy of the XPS spectrum which defines its chemical shifting. Chemical state analysis is frequently utilized for carbon. In roughly ascending order of increasing binding energy, it exposes the existence or absence of the chemical states of carbon such as in carbide, silane, amine, methylene, alcohol, ester, mono-di- and-tri fluoro-hydrocarbons.

Chemical state examination of a silicon wafer surface reveals chemical shifts caused by various formal oxidation states, including silicon suboxide, silicon monoxide, silicon dioxide, and n-doped and p-doped silicon (metallic silicon).

2.7 Hall Effect and Vander Pauw method

2.7.1 Hall Voltage and Lorentz Force

Analyzing the resistivity of a sample and Hall voltage are critical steps in semiconductor material study and testing. Bulk doping is the main factor that affects the resistivity of semiconductor materials. The capacitance, the resistance in series, and the threshold voltage of a component could all be impacted by resistivity. Hall voltage measurements are utilized to determine the mobility, free carrier density, and semiconductor nature either n-type or p-type as well as the doping level.

Lorentz force is the basic physics concept that underlies the Hall effect. The electron moving in a perpendicular direction to an applied magnetic field experiences a force acting normally in both directions and moves in response to the force produced by the internal electric field. Considering an electrically conducting material placed in a magnetic field $\vec{B}$ pointed in the $\hat{z}$ direction. Suppose we pass a current through that sample perpendicular to the magnetic field in the $\hat{x}$ direction. Then the free carriers in the sample experience a force $\vec{F}$ given by the Lorentz equation. The Lorentz force is expressed as:

$$\vec{F} = q(\vec{v} \times \vec{B})$$

where q is the charge of a carrier and $\vec{v}$ is the velocity as indicated below. Supposing the free charge carrier is an electron ($q = -e$), this causes the $+\hat{y}$ side of the sample to have an overabundance of negative charge. With this charge distribution, an electric field $\vec{E}_y$ directing in the $-\hat{y}$ direction is created, which keeps the Lorentz force and maintains the current flow in the $\hat{x}$ direction and yields a voltage difference $V_H = wE_y$ across a sample of width w . When we consider the forces acting on the free carriers in equilibrium:

$$\vec{F} = q(\vec{E}_y + [\vec{v} \times \vec{B}_z]) = 0$$

The electric field due to the Hall effect is thus expressed as

$$\vec{E}_y = -\vec{v} \times \vec{B}_z$$

The nature of a semiconductor sample can be known either as p-type or n-type by measuring the sign of the hall voltage V_H , since V_H is proportional to $\vec{E}_y$.

Assume that the sample charge carriers are electrons, making the semiconductor an n-type semiconductor. The current density in terms of the electron density n and average drift velocity v_x is given as $J_x = -env_x$ and the cross-sectional area $A = wt$. Then, the total current is $I_x = J_x A$. Therefore $I_x = -env_x(wt)$

The Hall voltage in terms of the width of the sample and the electric field as $V_H = wE_y$.

By substituting $w = \frac{I_x}{-env_x t}$ and $\vec{E}_y = -\vec{v} \times \vec{B}_z$, the hall voltage is:

$$V_H = \frac{I_x \vec{B}_z}{-ent}$$

2.7. 2 Hall Coefficient

The Hall coefficient is expressed as the ratio of the Hall Electric field E_y to the product of the current density and the magnetic flux density $\vec{B}_z$ is $R_H = \frac{E_y}{J_x \vec{B}_z}$ which is also expressed by the substitution of the hall electric field and the current density for an electron.

$$R_H = -\frac{1}{en}$$

2.7. 3 Resistivity

The study of electrical resistivity and conductivity of a material facilitates the relation of the potential gradient to the current flowing through it and to the current density. The resistivity of a semiconductor sample is given as:

$$\rho = \frac{1}{q(n\mu_n + p\mu_p)}$$

where n and p are the doping levels, μ_n and μ_p are the mobility of the majority carrier of electrons and holes respectively.

2.7.4 Hall Mobility

Mobility describes the relationship between the drift velocity and the applied electric field in a material. The mobility of electrons and holes with a drift velocity in $\hat{x}$ direction is:

$$\mu_e = -\frac{(V_e)_x}{E_x}$$

$$\mu_h = \frac{(V_h)_x}{E_x}$$

2.7.5 Vander Pauw Method

The van der Pauw approach is a well-known technique to determine sheet resistance and Hall coefficient of a sample along with the doping type, and the mobility, the majority of the charge carrier. Since Leo Johan Vander Pauw discovered the technique in 1958 [75], the method has become commonly utilized in the fields of electronics and solid-state and condensed matter physics, for instance, for determining semiconductor properties coupled with the Hall effect [76].

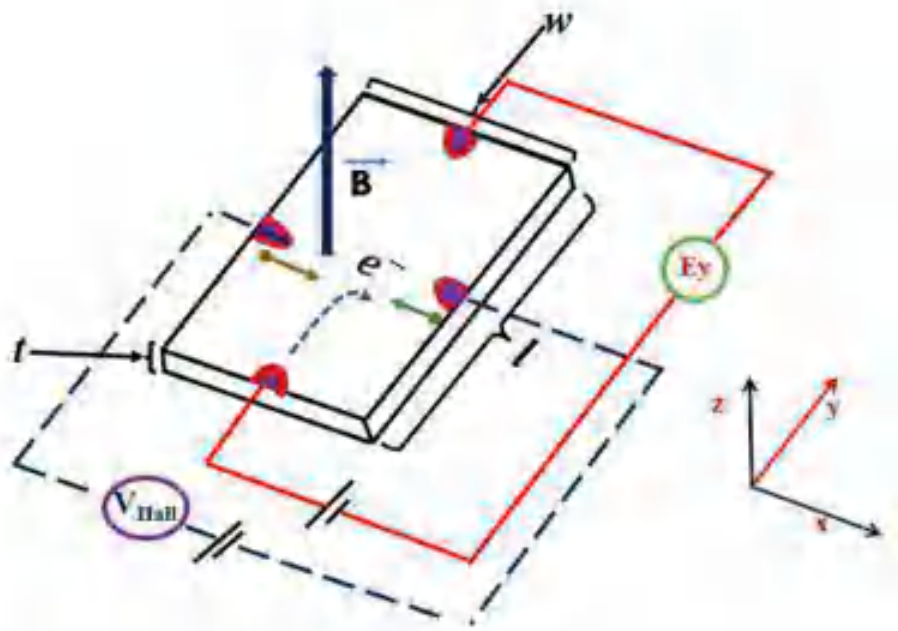


Figure 10: Van der Pauw Four-probe method

The method uses four probes; two probes are used to supply an electrical current while a voltage develops between the other two probes. The resistance developed along this combination is defined as R_a and the resistance developed by alternating the combination of probes for the current and voltage lead is defined as R_b . The Resistance $R_{ab, cd}$ of the potential difference developed between contact cd when an electric current J_{ab} flow from a to b in the Van der Pauw method is defined according to the relation $R_{ab, cd} = \frac{V_d - V_c}{I_{ab}}$.

The Van der Pauw formula according to the equation below is used to calculate the resistivity of the sample using the two resistances and the material thickness (t) [75].

$$\exp\left(\frac{-R_a}{k}\right) + \exp\left(\frac{-R_b}{k}\right) = 1$$

where $k = \frac{\rho}{\pi t}$, ρ is the resistivity of the sample and t is the sample thickness.

The prerequisite to be met for this approach is as follows:

- a) The sample needs to be plain and have the same thickness throughout.
- b) The sample needs to be isotropic and homogeneous.
- c) There should be no solitary holes in the sample.
- d) The four contact points must be centered at the edge of the sample.
- e) Any single point of contact is expected to have a contact surface area that is at least an order of size lower than the total sample surface area.

2.7.6 Contact Configuration

The configuration involves using four wires in which the two opposite wires were used to measure currents and the potential differences along the path respectively. Current is allowed to flow along one edge of the sample, while the voltage across the other edge is measured.

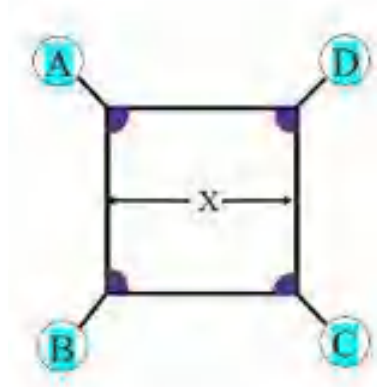


Figure 11: Contact Configuration

The current flowing along I_{AB} and voltage across the opposite edge V_{CD} can be used to calculate the resistance using Ohm's law defined as:

$$R_{AB,CD} = \frac{v_{CD}}{I_{AB}}$$

Van der Pauw demonstrated the use of resistance along the vertical edge for example $R_{AB,CD}$ and the horizontal edge $R_{BC,DA}$ are used to calculate the sample sheet resistance of an arbitrary shape. The accuracy of R_{ver} and R_{hor} is improved by considering the reciprocal theorem in defining the resistances.

We have from the reciprocity theorem that:

$$R_{AB,CD} = R_{CD,AB}$$

Now re-writing the resistances;

$$R_{ver} = \frac{R_{AB,CD} + R_{CD,AB}}{2}$$

$$R_{hor} = \frac{R_{BC,DA} + R_{DA,BC}}{2}$$

The accuracy of the sample resistance could even be improved by switching the polarities of the current source and voltage across it. The average resistivity is thus expressed as:

$$\rho = R_s \cdot t$$

where t is the sample thickness and R_s is the sheet resistance.

2.7.7 Electrical Resistivity Measurement

The use of thin film materials in high-technological applications for engineering has sparked global interest, increasing the demand for testing methods to spot odd electrical and thermal abnormalities in the materials. The chemical, electrical resistance, and thermal barrier potential have opened a wide range of applications for appealing physical, electrical, and mechanical properties for various industrial applications that are continually expanding. Electrical resistivity is a sensitive measure of modification in the physics of chemical binding, typically inversely proportional to the carrier density and electron mobility. Much research about the transport characteristics of films has been conducted since the discovery of the thermos-electric conducting properties of chemical compounds. The development of distinctive scientific applications made possible by recent advancements in measurement technology and tools has also resulted in exciting developments in the realm of material science. The measure of the temperature dependence electrical resistance is an essential tool for explaining the physics of the ground state, phases, electrical, electronic, and magnetic features, and oscillations identified in the examined materials for this specific kind of improvement.

2.7.8 Sheet Resistance

Sheet resistance (R_s) is an essential electrical characteristic utilized to describe the properties of conducting and semiconducting material thin films. It defined the resistance of a square piece of thin material with connections on its two opposing sides [77]. The resistance estimates the capacity of charged electron positioning in the film plane to measure the overall lateral resistance in respective of the covered area on the film. It is frequently used to characterize materials produced by metal deposition, semiconductor doping, glass coating, and a lot more.

2.8 Electrochemical Characterization (Basics of electrochemical workstation)

Over the past few decades, supercapacitors have been the subject of extensive research and have emerged as essential energy storage components for microelectromechanical systems. Promising options because of the exceptional conductivity and good cycling stability make transition metals have a high potential for supercapacitor electrodes. The various electrochemical characterization

techniques involving cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy are essential to quantify the electrochemical behavior. A key factor in the overall performance of supercapacitors is the appropriate choice of the compatible electrode, electrolyte, separator, and current collector [78]. Aqueous electrolyte solution and concentration proffers different ionic conductivity and compatibility mechanisms with the working potential. An essential component of electrochemical supercapacitors is the electrolyte, which is defined as the salt of electrolyte plus solvent. Their influence on the double layer's development and the pores' accessibility to electrolyte ions is noteworthy. Therefore, while fabricating high-performance supercapacitors, selecting the ideal electrolyte is crucial. Greater chemical and electrochemical stabilities in electrolytes allow for larger potential windows without sacrificing functionality. For electrolyte materials to help ensure the safe operation of electrostatic sensors, they ought to be minimally flammable, volatile, and prone to corrosion. Ion concentration, solvent type, ion-solvent interaction, electrode-to-electrolyte interaction, potential voltage window, and ion size and type are all components of the electrolyte nature [79]. Aqueous electrolytes have been generally used in experimentations because they are simpler to work with in the laboratory than organic electrolytes and ionic liquids, which require purification [80,81]. When compared to organic and ionic liquid electrolytes, aqueous electrolytes usually have conductivities that are at least one order of higher magnitude. Improved power density and lower equivalent series resistance (ESR) are two benefits of high conductivity. The widely popular aqueous electrolytes include tetraoxosulphate (vi) acid (H_2SO_4), potassium hydroxide (KOH), sodium tetraoxosulphate (vi), and potassium chloride (KCl). They offer low ionic resistance and are simple to handle in an open atmosphere [82,83]. The capacitance, power density, energy density, and cycle life of the supercapacitors are all significantly impacted by these parameters. Transition metal oxides, conducting polymers, carbon nanotubes, graphene, and activated carbon are examples of frequently used electrode materials. The electrodes can be connected as two or three electrodes setup as illustrated in Figure 12. Another key component is the separator material such as paper, glass, and ceramics which forbids electron transfer between the electrodes. To ensure device dependability and prevent active materials movement over time, a separator needs to be mechanically strong. The introduction of additional resistance lowers the performance of the separator. Therefore, it is enjoined and essential to select an appropriate separator compatible with the electrolyte and the electrodes, especially with the features of being chemically resistant to the

electrolyte, possessing electronic insulation characteristics, non-conductive nature, and superior ionic conductance.

2.8.1 Cyclic Voltammetry

Cyclic voltammetry is an electrochemical technique used to measure the current response of a redox-active solution to a linearly cycled potential sweep. It is a useful method to quickly determine information about the thermodynamics of redox processes, the energy levels of the analyte, and the kinetics of electronic-transfer reactions.

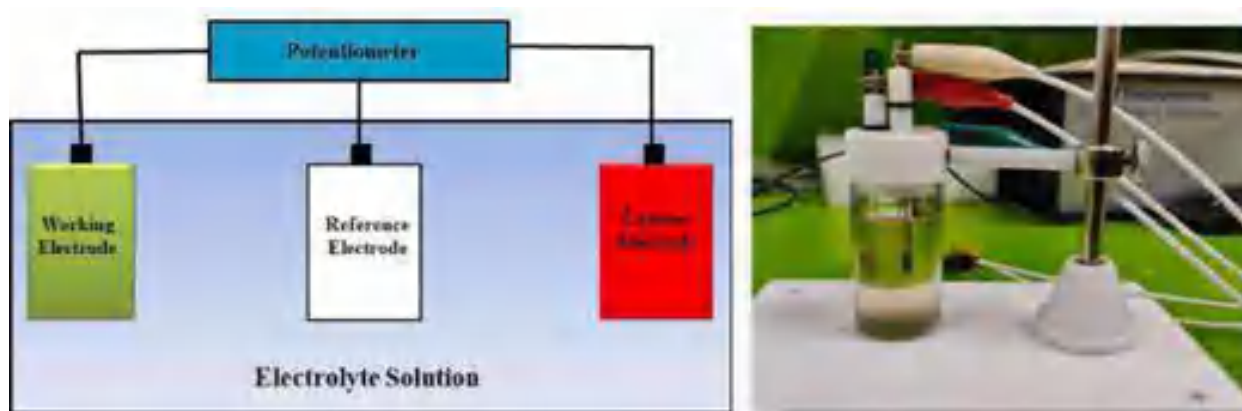


Figure 12: Three electrodes setup [84]

It is an advanced voltammetry and potentiometric technique. It is a useful method to assess a redox-active solution's current responsiveness and record the current versus potential. A technique for determining an electrochemical cell's electric potential in a static environment is potentiometry. In voltammetry, on the other hand, the current is measured while the potential between two electrodes is adjusted [85,86].

The techniques involve the use of three electrode systems: the working electrode, a reference electrode, and a counter electrode. A potentiostat linearly sweeps the potential between the working electrode and a reference electrode and then sweeps back after the preset limit. The procedure is repeated several times during the scan. The changing current between the working electrode and the counter probes results in a characteristic cyclic voltammogram plot.

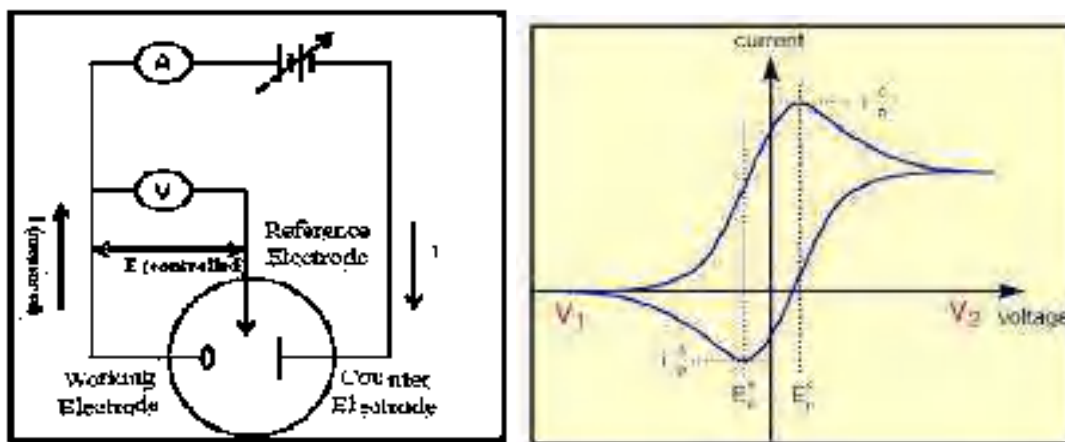


Figure 13: Cyclic Voltammetry Circuit Set Up and Cyclic Voltammogram [87]

2.8.2 Galvanostatic Charge Discharge

Galvanostatic charge-discharge is one of the methods of determining electrochemical behavior. It is often used to measure the energy stored in electrochemical capacitors and other materials. The technique recharges and discharges material up to the preset possible threshold by applying continuous positive and negative currents repeated for several cycles. GCD data is also used to determine specific capacitance, energy density, and power density. GCD profiles are typically employed and used to derive several important terms such as capacitance, energy density, and power density that are used in assessing the capacitance quality and detecting the presence of irreversible Faradaic reaction. The GCD profiles of an EDLC material are linear indicating good electrochemical behavior while the GCD curves of a pseudocapacitor have a non-linear charge-discharge profile due to quasi-reversible faradic reactions [88,89].

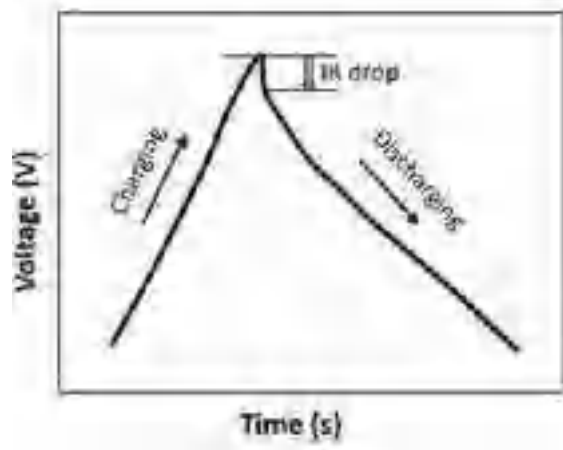


Figure 14: GCD graph

2.8.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy is a unique non-destructive electrochemical method employed to examine various devices in diverse energy storage applications by measuring the system impedance frequency of an alternating current. Electrochemical cell impedance can be identified by EIS. The electrode setup can be subjected to a relatively small sinusoidal voltage to measure impedance. This will generate an electric current for which the sinusoidal voltage's phase angle and amplitude are measured. The application of EIS includes its high surface sensitivity, electrode characterization in a storage mechanism, detection of several changes such as variation in polymer layers, surface change to protein absorption or corrosion protective layer penetration, and component separation effects such as electron transfer resistance, and double layer capacitance. EIS data can be interpreted by using an Equivalent Electrical Circuit element, in which spectra are expressed as combinations of circuit components like resistors, capacitors, and inductors. The mentioned components determine the system charge transfer resistance and double-layer capacitance. Other components are Warburg Impedance and constant phase elements that are not analogous to the basic electric circuit. The Warburg Impedance is created because of diffusion, and it is more pronounced at a low frequency. The real impedance (Z_{real}) and imaginary impedance (Z_{imag}) are the basic types of impedance in EIS. By providing a potential wave to the working electrode and observing the ensuing current wave, the impedance can be determined. The electrochemical process associated with the electrolyte and redox reaction is evaluated as an equivalent circuit, which comprises the resistors, capacitors, and inductors, and the circuit

evaluates each of the EIS system components. The resistance of the solution (R_s), double layer capacitance at the electrode surface (C_{dl}), charge transfer resistance (R_{ct}), and Warburg resistance (Z_w), are simplified in the combined equivalent circuit [84,90]. Finally, a constant phase element is introduced to model the non-ideal capacitor behavior.

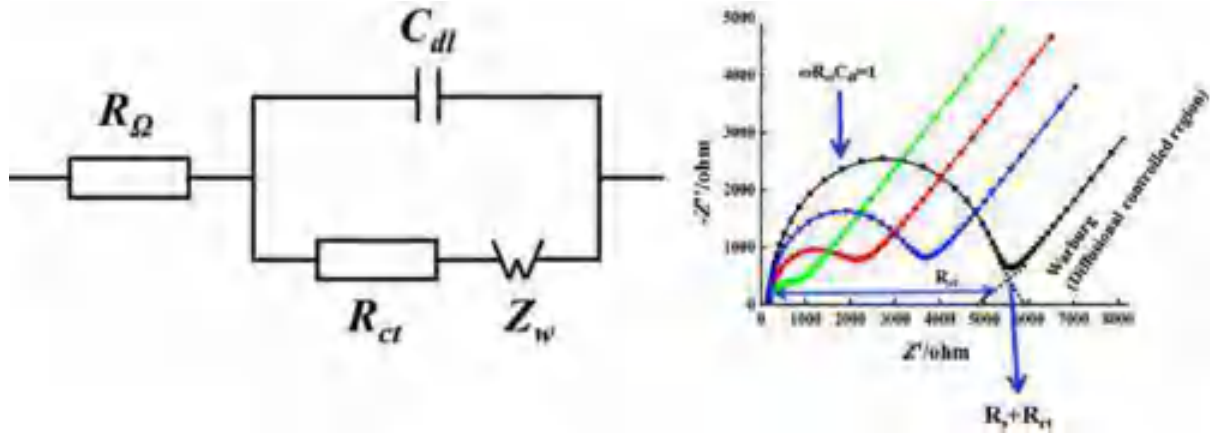


Figure 15: EIS circuit and Randle equivalent circuit for the electrochemical system [91]

CHAPTER 3

SYNTHESIS AND STUDY OF CHROMIUM NITRIDE AND CHROMIUM OXYNITRIDE THIN FILMS

3.1 Experimental Details and Methodology

The chromium nitride and chromium oxynitride thin films have been grown by using radio frequency magnetron sputtering. The films were fabricated on Si(001) and fused silica substrates. The substrates went through a thorough cleaning procedure before deposition, which included ex-situ sonication with acetone and then methanol to guarantee the elimination of any surface impurities that might have an impact on the growth and quality of the film.

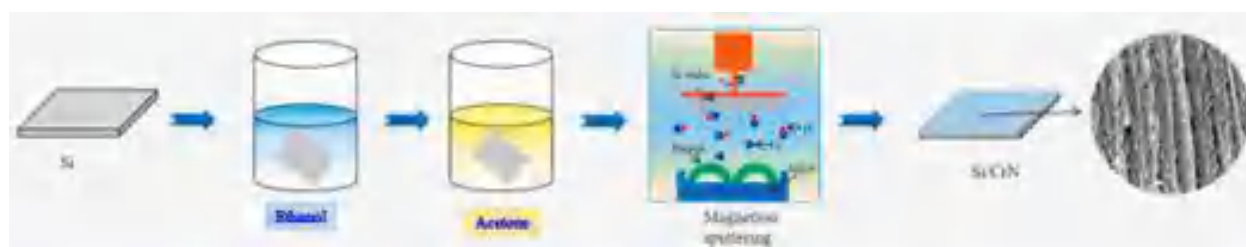


Figure 16: Schematic fabrication process of film [92]

After cleaning, the substrates were put inside the sputtering chamber, which was then evacuated to produce an ideal vacuum environment for film deposition: a base pressure of 7.6×10^{-6} Torr after several hours of continuous pumping. The Si(001) and glass were held at room temperature and constantly rotated at six revolutions per minute (rpm) for consistent film growth mode on the substrate during the deposition. The Cr flux was generated from a high purity (99.99%) Cr target, and nitrogen (99.999%) and oxygen (99.999%) were supplied as reactive gases. The high-purity (99.99%) chromium (Cr) material was selected for sputtering because it can serve as a pure supply of chromium for the creation of CrN films. During the sputtering process, reactive gas, nitrogen and oxygen, and processing gas; argon was injected into the chamber. To examine its effect on the film characteristics, the nitrogen flow rate, oxygen flow rate, and argon flow rate's total growth recipe pressure are kept constant while the flow rates of each of the processing and reactive gas are varied in all the films and deposition time essential in the formation of the CrN and $\text{CrN}_x\text{O}_{x-1}$ compounds was varied. A 50 sccm total growth recipe pressure was maintained in all the films

because at this pressure, a stable plasma is formed, and a high-quality thin film is guaranteed. The radiofrequency power is maintained throughout all samples. A crystal thickness monitor, which provides exact control over the deposition rate and film thickness, was used to measure the film thickness in real-time throughout the growth procedures. Once the film completed growth to a certain thickness, the samples were cooled down to room temperature before venting the growth chamber. Similarly, for growing chromium oxynitride samples, along with nitrogen, oxygen gas has been introduced to the chamber. The oxygen flow was controlled according to the desired oxygen concentration in the films. Table I shows the growth parameters and film thicknesses grown by the sputtering system. After growing the films, their thickness was measured by a Dektak XT profilometer.

Table 1: Growth parameters of the films

Film	Ar flow (sccm)	N ₂ flow (sccm)	O ₂ flow (sccm)	Chamber Pressure (Torr)	RF power (W)	Rotation (rpm)	Film thickness (nm)
F1	50	0	0	7.66×10^{-3}	125	6	233
F2	49	1	0	7.38×10^{-3}	125	6	242
F3	48	2	0	5.65×10^{-3}	125	6	101
F4	46	4	0	7.40×10^{-3}	125	6	51
F5	45	5	0	7.80×10^{-3}	125	6	45
F6	44	6	0	7.66×10^{-3}	125	6	336
F7	46	2	2	7.50×10^{-3}	125	6	116
F3 *	48	2	0	5.11×10^{-3}	125	6	250

3.2 Results and Discussion

3.2.1 Sample Deposition Rate

The result of the deposition rate of the films is presented in Table 2 and **Error! Reference source not found.** below. Increasing the nitrogen flow rate to the sample growth mechanism decreases the deposition rate from samples F1 to F4. Further increasing the nitrogen flow from F5 to F6 leads to an increase in the deposition rate of the film due to a saturated influx of nitrogen in the chamber and a long growth time.

Table 2: Film deposition rate and growth time

Film	Thickness (nm)	Growth time (min)	Deposition rate (nm/min.)	bandgap (± 0.1) (eV)
F1	233	30	7.77	0.27
F2	242	35	6.91	1.63
F3	101	35	2.89	2.49
F4	51	40	1.28	2.60
F5	45	35	1.29	2.65
F6	336	50	6.72	2.18
F7	116	60	1.93	3.63
F3 *	250	20	12.5	2.48

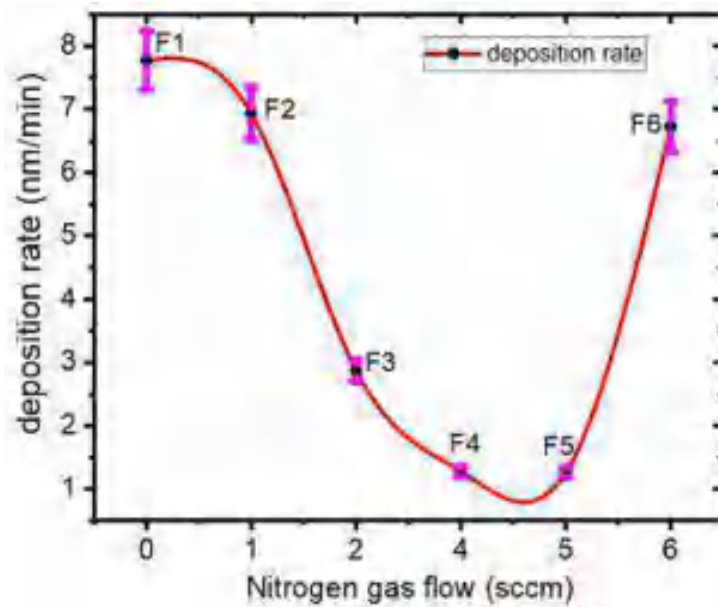


Figure 17: Sample deposition rate on the nitrogen flow

The variation of the processing gas flow rate, reactive gas flow rate, deposition rate, and measured thickness contribute to the changes in the obtained film properties. This changing mechanism is different between the films. For example, Films F1 to F5 showed a progressive decrease in the thickness and deposition rate along with a decreasing argon flow rate and an increasing nitrogen flow rate. Comparison of Samples F3 and F1 with Argon to Nitrogen flow rates of (Ar: N₂; 48:2) and (Ar: N₂; 50:0) respectively, it can be depicted that increasing argon gas flow rate and decreasing nitrogen flow rate, increases the deposition rate but decreases the thickness of the thin film with decreasing growth time. The compared result of the data showed that a decrease in argon flow rate, increasing/decreasing nitrogen flow rate, and increasing growth time caused a decrease in the deposition rate and thickness of the thin film. This depicts that the stoichiometry rule contributes majorly to the effects.

Generally, increasing the Ar flow rate increases both thickness and deposition rate but at a specific flow rate. When the Ar gas is flown into the chamber, the gas collides with an electron and loses an electron due to the collision and thereby becomes positively charged and is converted to ionize the gas. This accelerated upward with kinetic energy, $U = e\Delta V$ to bombard the surface of the

target sample with a high-energy particle of plasma. This continuum, with more Ar gas released into the chamber, and bombardment of the ionized gas, resulted in a high deposition rate and thin films. When the chamber is saturated with Ar gas, the particles of the gas collide with each other rather than bombard the surface of the target sample and eventually decrease the thickness of the films and the deposition rates as seen increasing flow rate of Ar gas on the thickness and deposition rate graph occurred between 47:3 to 50:0 sccm flow rate.

3.2.2 Structural Analysis

Powder X-ray diffraction (XRD) Bruker mode No: D2 phaser 2nd Generation and Rigaku mode No: Ultima IV was used to determine the crystal structure, phase orientation, and the crystallite size of CrN and CrN_xO_{1-x} thin films. Measurements were performed in the Bragg-Brentano (θ -2 θ) configuration, utilizing copper K α radiation (wavelength of Cu = 1.1541 Å) over a 2 θ range of 20° to 90°. This analysis facilitated the identification of crystalline phases and the calculation of lattice constants, offering a window into the structural integrity and the influence of growth conditions on the films. The XRD scans were conducted and compared to the Powder Diffraction Files (JCPDS) provided by the International Centre for Diffraction Data (ICDD) and references from literature to ascertain the crystallographic structure, phase compositions, and lattice constants of the films. The current and voltage excitation were set at 30mA and 40kV range respectively in the diffractometer. The crystal size of the films is determined from the average of the full width at half maximum (FWHM) of the resulting peaks of the XRD analysis obtained from the origin software for the corresponding (hkl) plane. The crystallite size of the films was calculated using Scherrer's equation (Cullity *et al* 1977) defined as:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where k , D , λ , β are constant, which is equal to 0.9, the crystallite size along the normal direction, the wavelength of the X-ray, the Bragg angle, and the full width at half maxima respectively. The angle of the k_α and k_β were obtained by substituting the corresponding values of the k_α and k_β of the XRD in the relation:

$$\text{From Bragg law: } n\lambda = 2d \sin \theta$$

$$n\lambda_{k_\alpha} = 2 d \sin \theta_\alpha$$

$$\sin \theta_\beta = \frac{2 d \sin \theta_\alpha n \lambda_{k_\beta}}{2 d n \lambda_{k_\alpha}}$$

Considering second-order diffraction and substituting the wavelength of k_α and respective 2θ ; The value of the k_β peak location is measured and calculated as expressed above.

Shown in Figure 18 (a-h) are the XRD patterns of CrN and CrN_xO_{x-1} thin films grown on Si(001) and glass substrates at varied argon flow rates as processing gas and nitrogen and oxygen as reactive gases. For all grown samples, the diffractogram indicates the main peaks referring to the Silicon peaks of Si (004) k_α at approximately $2\theta = 68.8^\circ$, and Si (004) k_β at approximately $2\theta = 61.3^\circ$. XRD spectra of samples F1, F2, F4, F5, and F6 of silicon (001) samples indicate the presence of the CrN (002) peak at $2\theta = 43.6^\circ$. Hexagonal phase (β -Cr₂N) peaks are present in F1, F6 and F7. Chromium nitride (CrN) peaks are not discovered in samples F3 and F3* because of the low chamber pressure of 5.65×10^{-3} Torr and 5.11×10^{-3} Torr respectively, and thereby reduced the free mean path to sustain the deposition of the sputtered atoms. Sample F1 shows a structural phase transition of the hexagonal phase (β -Cr₂N) peaks of (002) and (111) at $2\theta = 39.7^\circ$ and $2\theta = 42.8^\circ$ respectively. Sample F1 only shows a hexagonal phase (β -Cr₂N) peak of (201) at $2\theta = 48.3^\circ$ while sample F7 a structural phase transition of the hexagonal phase (β -Cr₂N) peaks of (011) and (111) at $2\theta = 29.4^\circ$ and $2\theta = 42.8^\circ$ respectively. Both samples F1 and F7 show a hexagonal phase (β -Cr₂N) peak of (111) and at $2\theta = 42.8^\circ$ indicating the influence of high oxygen residual gas and high oxygen flow concentration presence in the chamber respectively. Structural phase transitions of Cr₂O₃ peaks occur in sample F7 of (003), (012), and (008) at $2\theta = 18.5^\circ$, 41.8° , and 52.9° respectively, and a structural phase transition of SiO₂ peaks of (001) and (022) at $2\theta = 21.8^\circ$ and $2\theta = 39.7^\circ$ respectively. This is the only sample grown with oxygen incorporated. Silicon nitride (Si₃N₄) peak of phase (002) at $2\theta = 26.5^\circ$ and a silicon peak of phase (002) at $2\theta = 32.9^\circ$ also emerges in sample F7. Structural crystal system transition of SiO₂ of phase (002) peak triclinic crystal system and structural phase transitions of SiO₂ of phase (311) peak monoclinic crystal system occur in sample F6, which established the presence of high nitrogen flow concentration. There is a presence of numerous silicon (iv) oxide (SiO₂) in sample F1 due to the zero concentration of nitrogen in the chamber, the chamber is overwhelmed by the oxygen residual gas.

Both samples F3 and F3* have the same argon and nitrogen growth parameters but different chamber pressures, the thin F3* showed the presence of Si (002) peak at $2\theta = 32.9^\circ$ while the peak was absent in thin films F3.

Figure 18 (i) shows the XRD diffraction pattern of the thin film grown on glass at different flow rates of argon as processing gas and nitrogen and oxygen as reactive gases. For all grown samples, there is no noticeable peak on the glass substrate because the substance is amorphous but there is a brag bump on samples F2, F3, and F4 while samples F1, F5, F6, and F7 show a small peak around $2\theta = 24.7^\circ$ which could be the presence of the SiO_2 compound on the sample surface.

Table 3: Compound's lattice constant and crystallite size

Sample	Compound	Peak	2θ (degree)	Si (004) Peak (degree)	Lattice constant (Å)	Crystallite size (nm)
F1	CrN	002	43.68°	69.15°	4.144	216
F2	CrN	002	43.67°	69.09°	4.145	214
F4	CrN	002	43.92°	69.14°	4.123	218
F5	CrN	002	43.72°	68.94°	4.141	213
F6	CrN	002	43.94°	69.14°	4.121	122

The changes in the lattice constants and the crystallite size of the films are due to tensile stress imposed by the residual gas. The corresponding silicon peak 2θ of the films is decreasing along with the increasing nitrogen low rate, reducing the full width at half maxima, and increasing the spacing of the interplanar atoms and the crystallite size of the films.

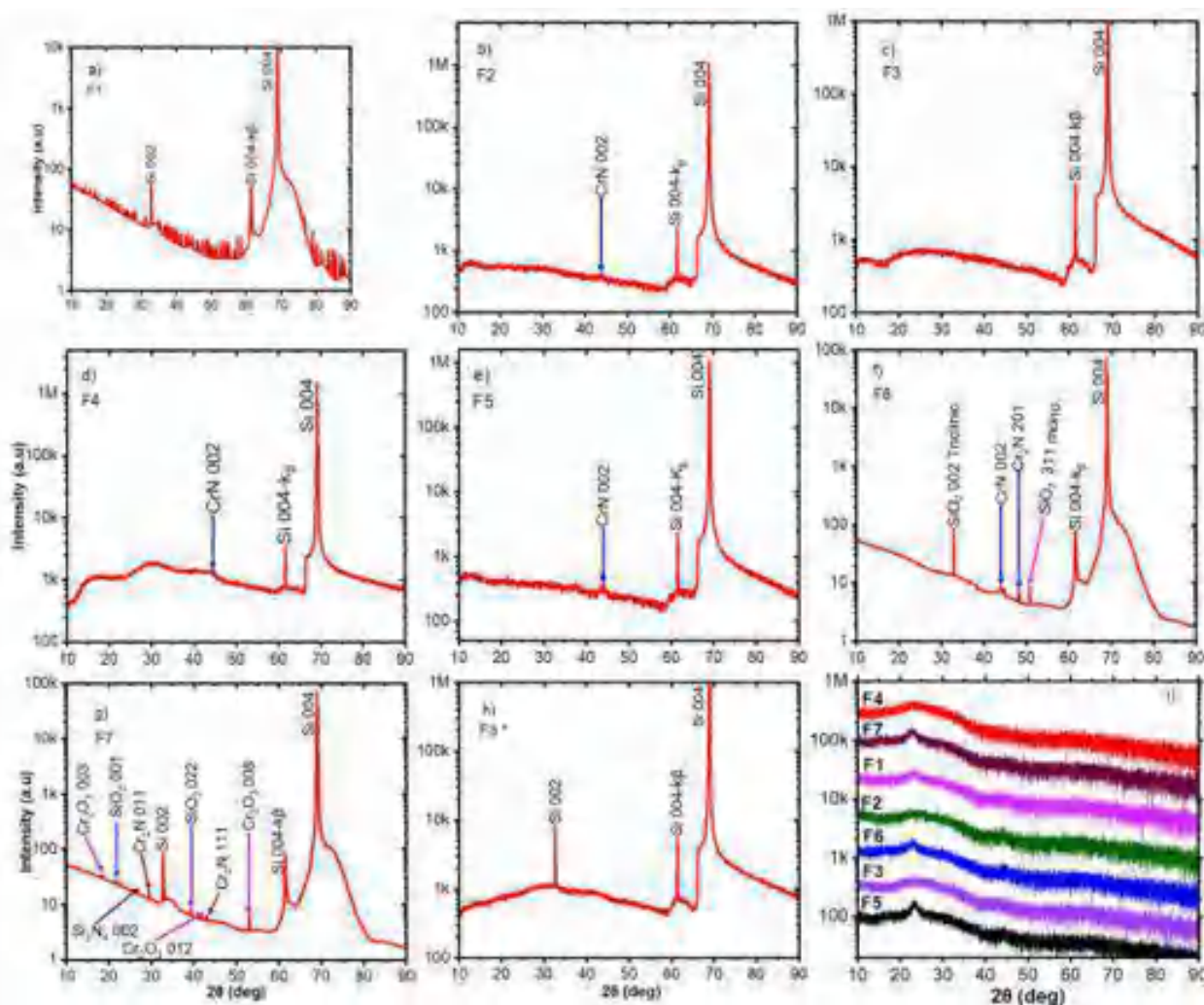


Figure 18: XRD patterns for Si(001) and glass substrate thin films

3.2.3 Composition and Topography Analysis

A scanning electron microscope (SEM) is a microscopy type of instrument that uses an electron interaction with the atoms of the sample to create figures of the sample by scanning the surface with beams of incident electrons. In SEM analysis, the topography and the chemical composition of the films are revealed due to the interaction of electrons with the atoms of the samples. An image is created by combining the position of the electron beam with the counts of intensity per second of the signal that is captured while it is being scanned in a raster scan mode. A secondary electron detector quantifies the secondary electrons that are released by excited atoms in the most popular SEM mode. In this study, an SEM model: JEOL JSM 6610LV is employed to investigate the composition and the topography of the thin films with an applied voltage of 20kv and magnify

between 10,000 to 50,000 μm to detect the flaws in the samples. The SEM figure of the thin films is presented in Figure 19.

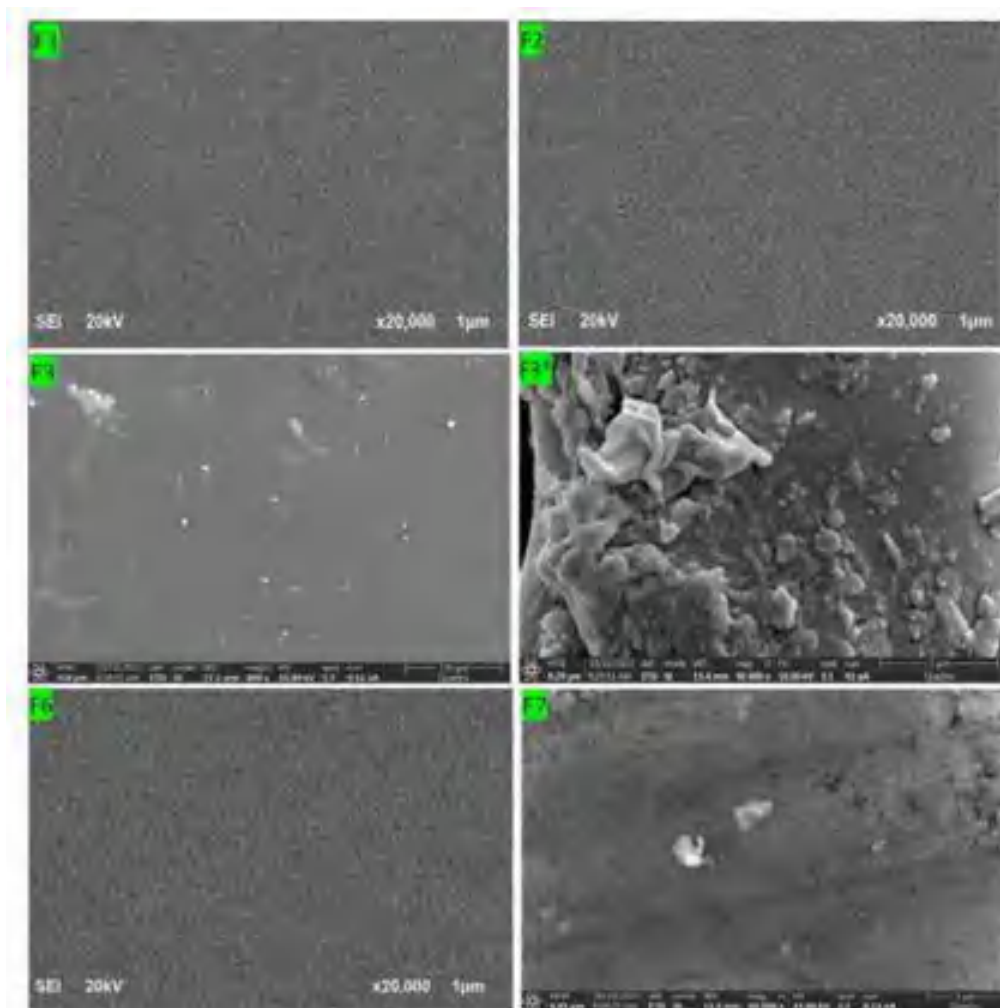


Figure 19: SEM pattern of F1, F2, F3, F3*, F6, and F7

3.2.4 Elemental Analysis and Cross-Section Characterizations

Energy dispersive X-ray spectroscopy (EDX) is a qualitative and quantitative method for characterizing the chemical composition or elemental constituents of a sample. The lateral disposition of elements from the region of imaging may be mapped out using the EDS analysis, which can also be used to establish the elemental composition of specific sites. The figures below show the EDX analysis of the activated samples.

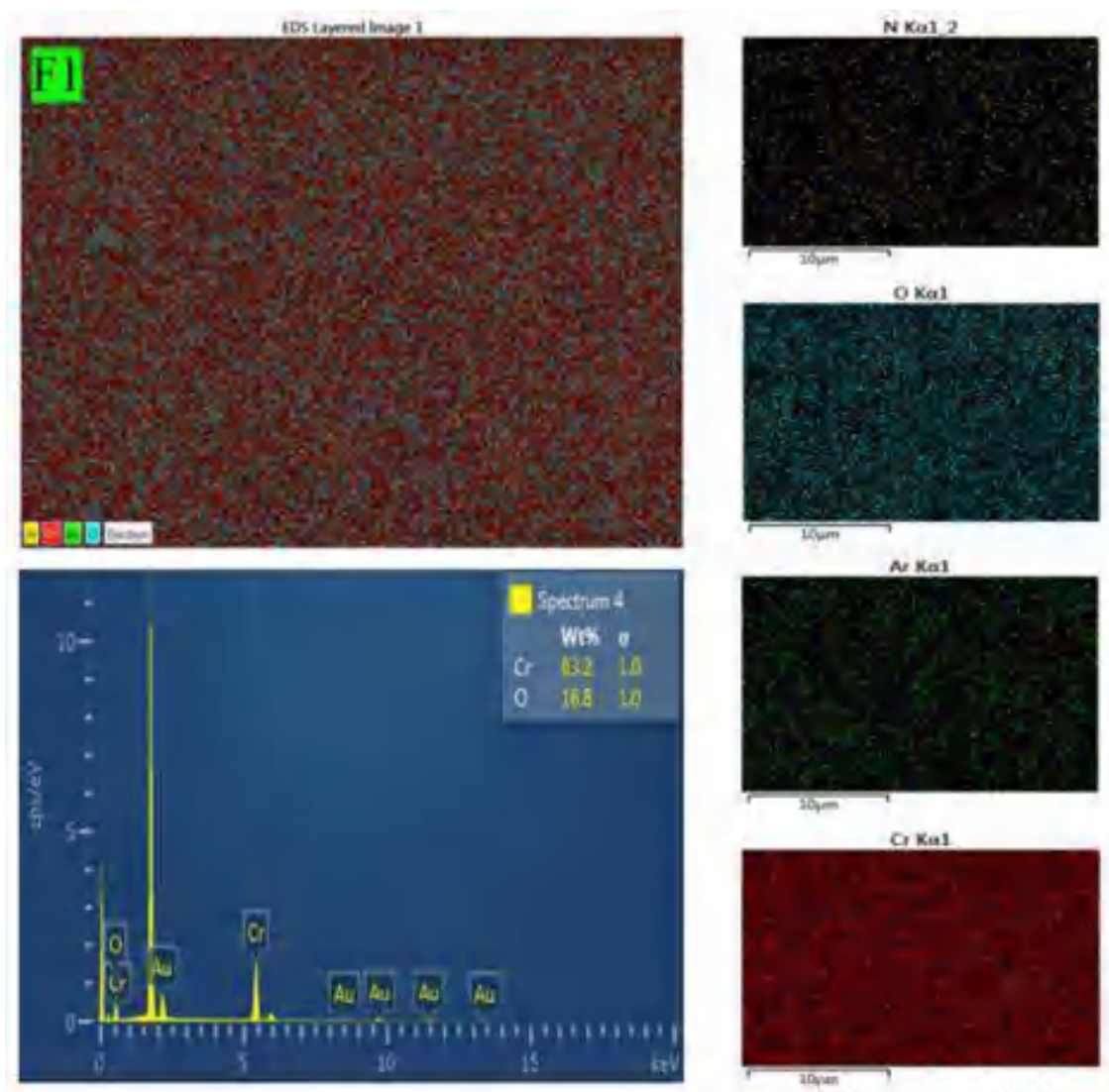


Figure 20: EDS of the layered image of sample F1

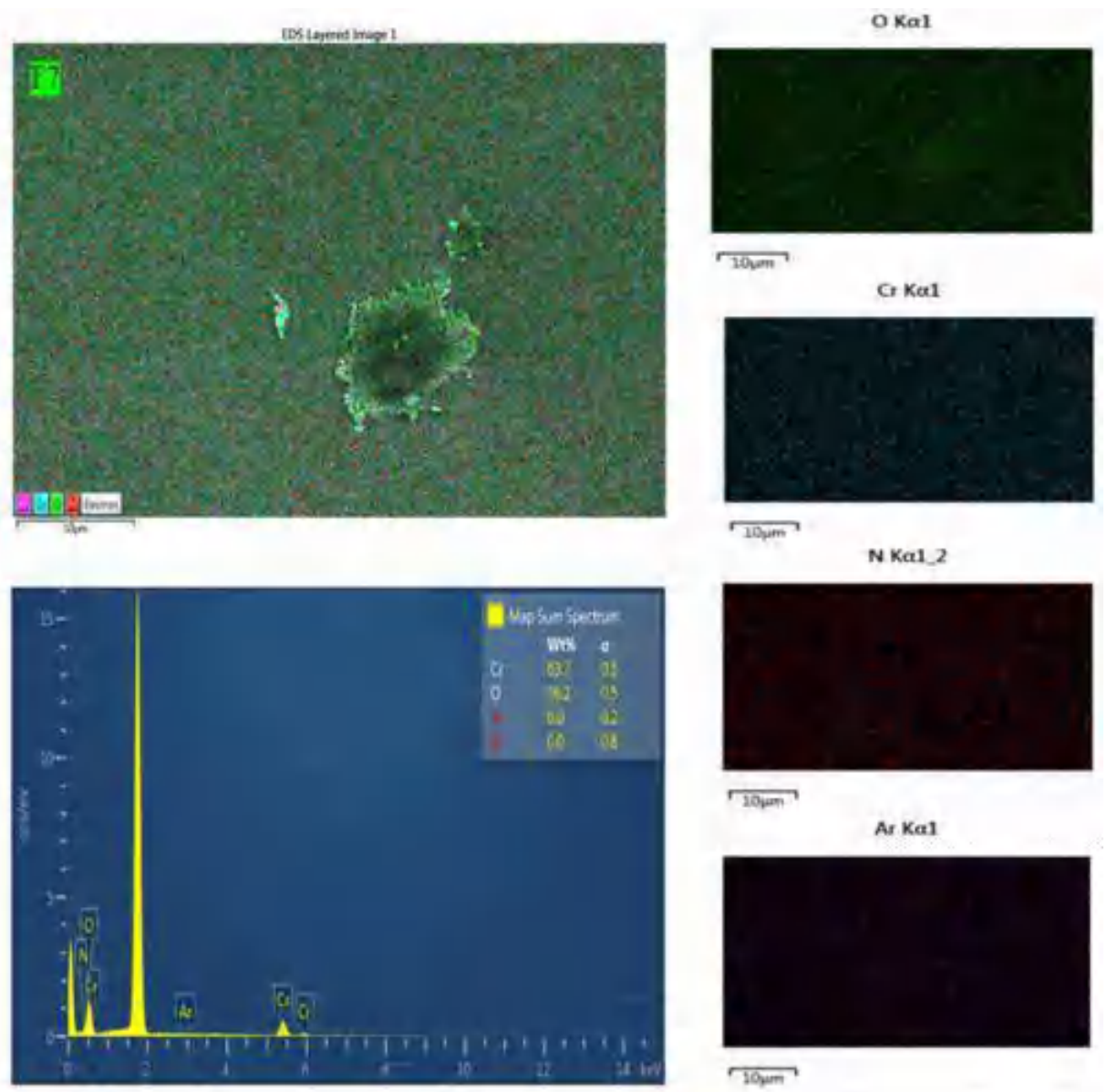


Figure 22: EDS of the layered image of sample F7

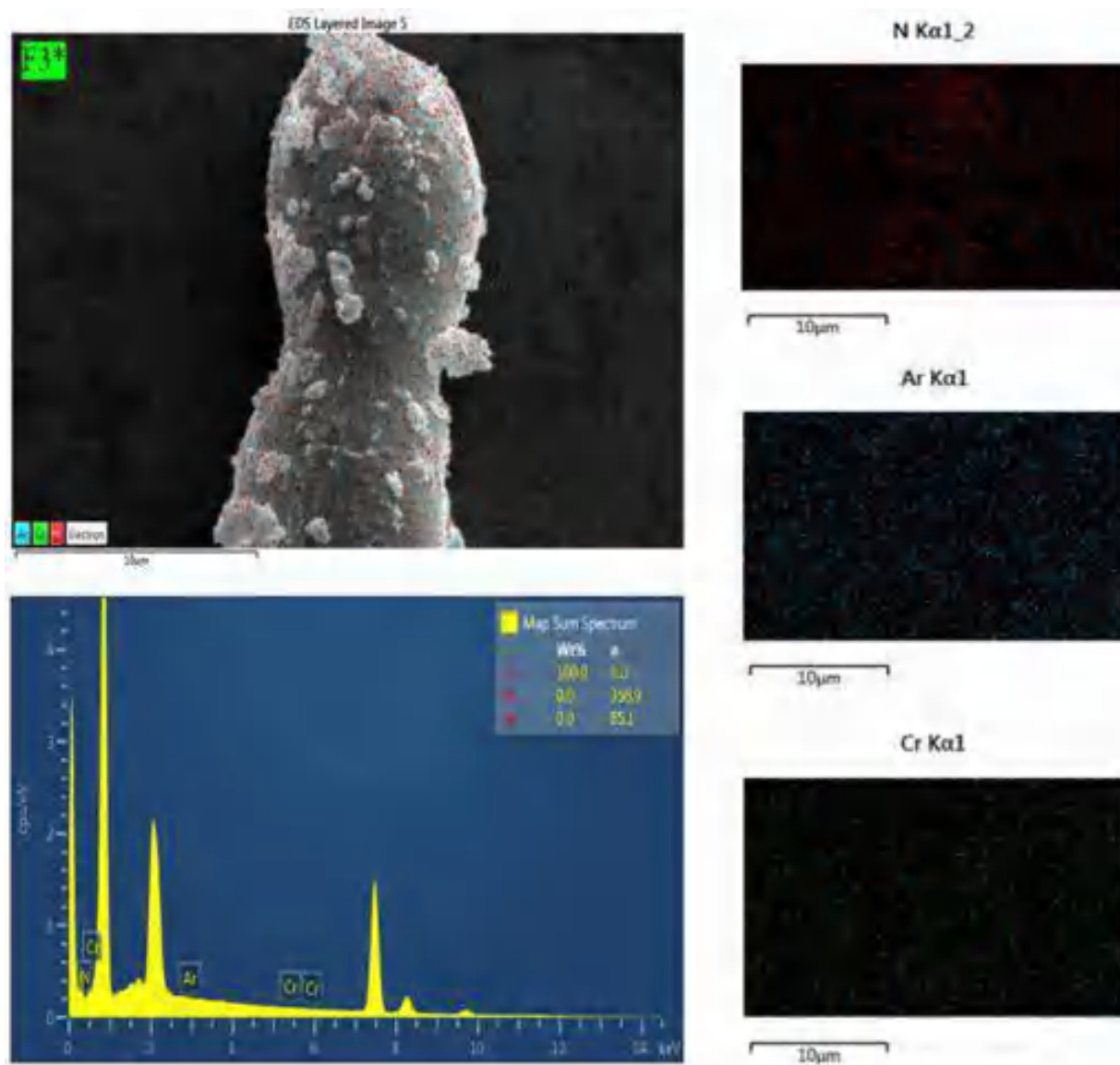


Figure 23: EDS of the layered image of sample F3*

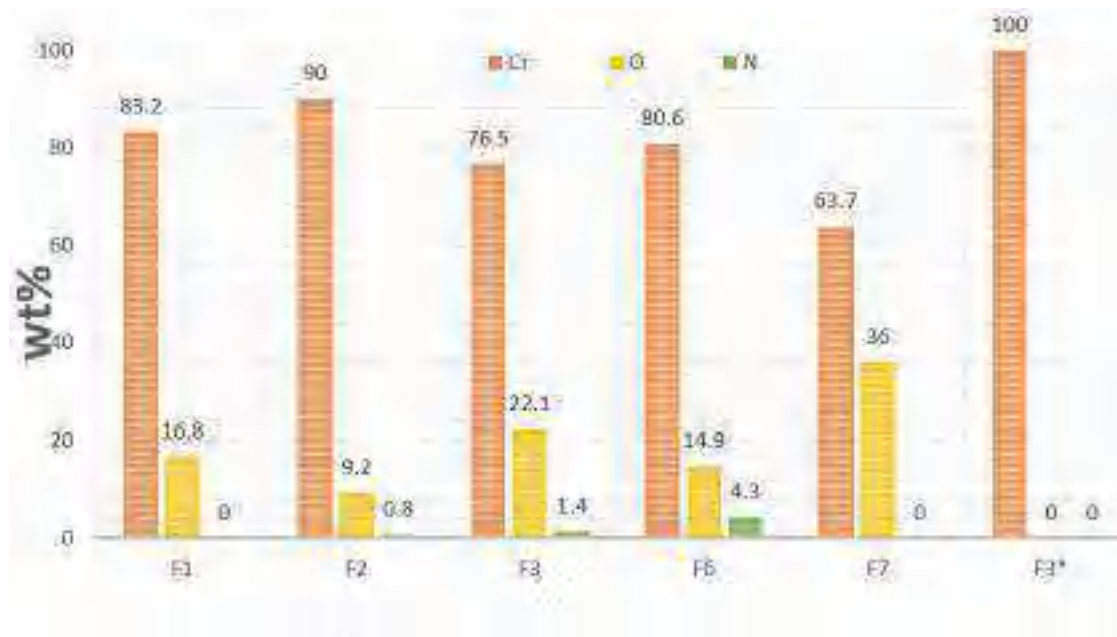


Figure 24: Weight percent of map sum spectrum of samples F1, F2, F3, F6, F7, and F3*

The cross-section of the sample F2, F3, and F5 figure is given below. In the analysis, the various percentage contributions of the individual element were revealed.

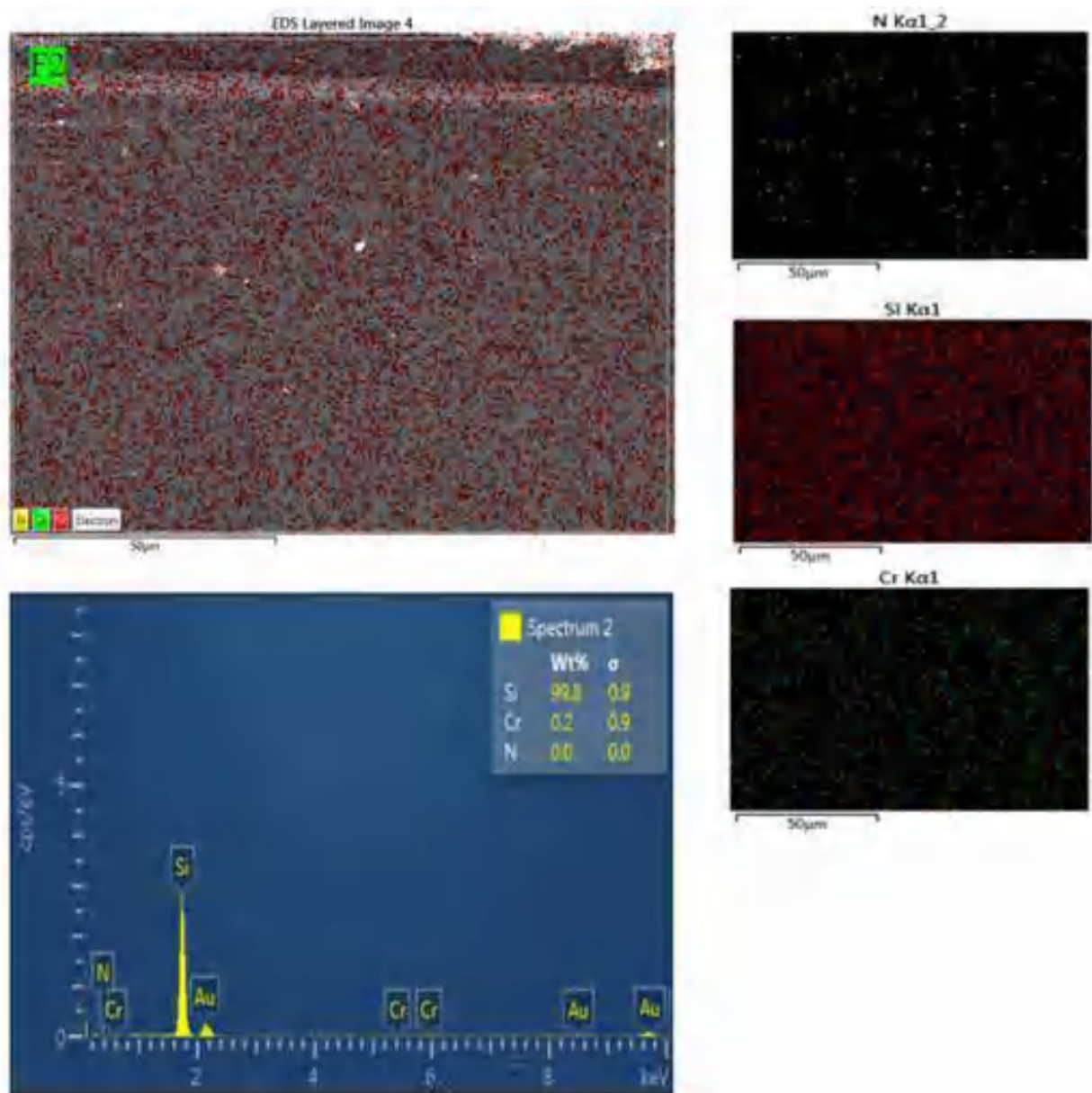


Figure 25: Cross-section EDS of the layered image of sample F2

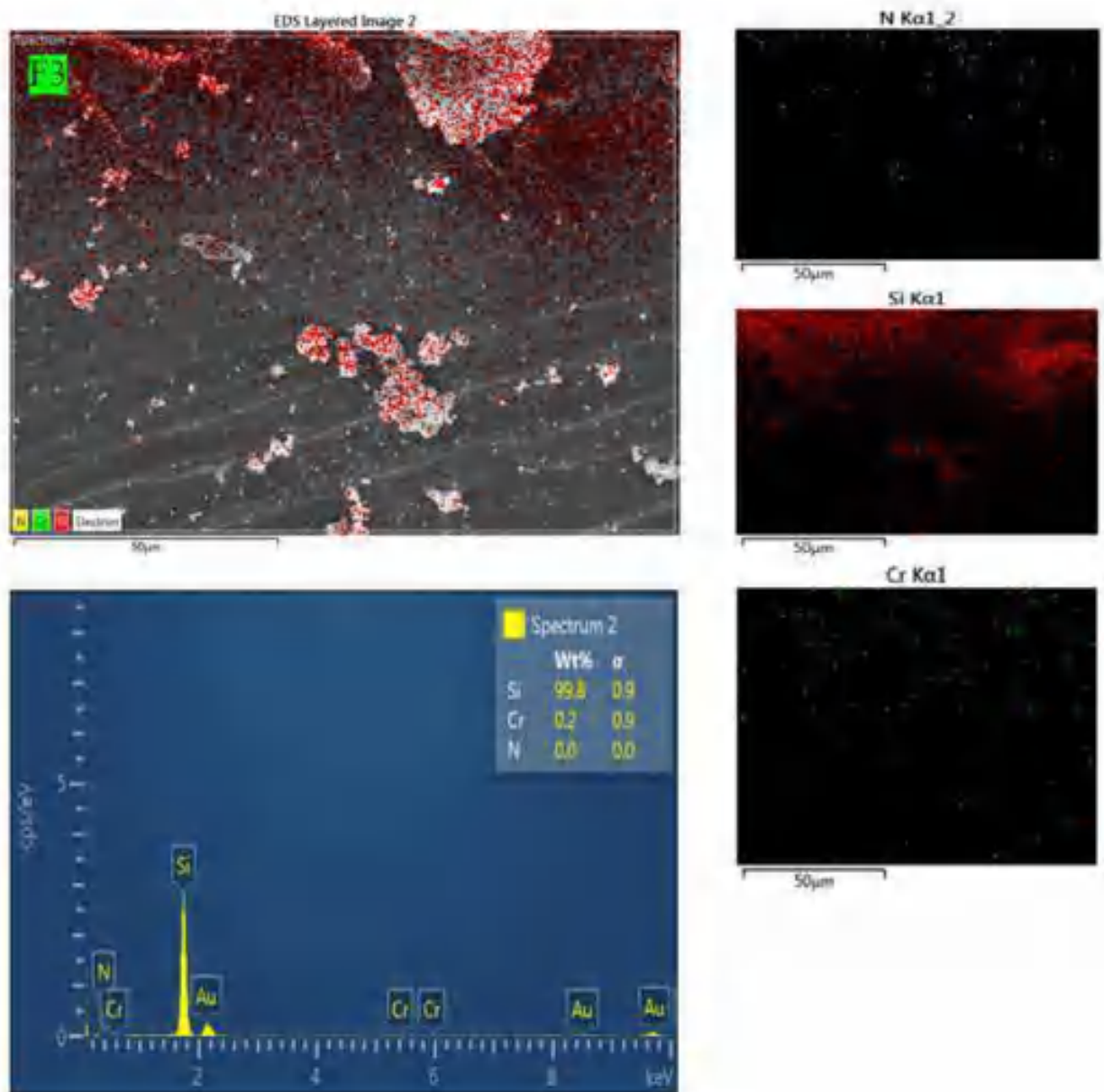


Figure 26: Cross-section EDS of the layered image of sample F3

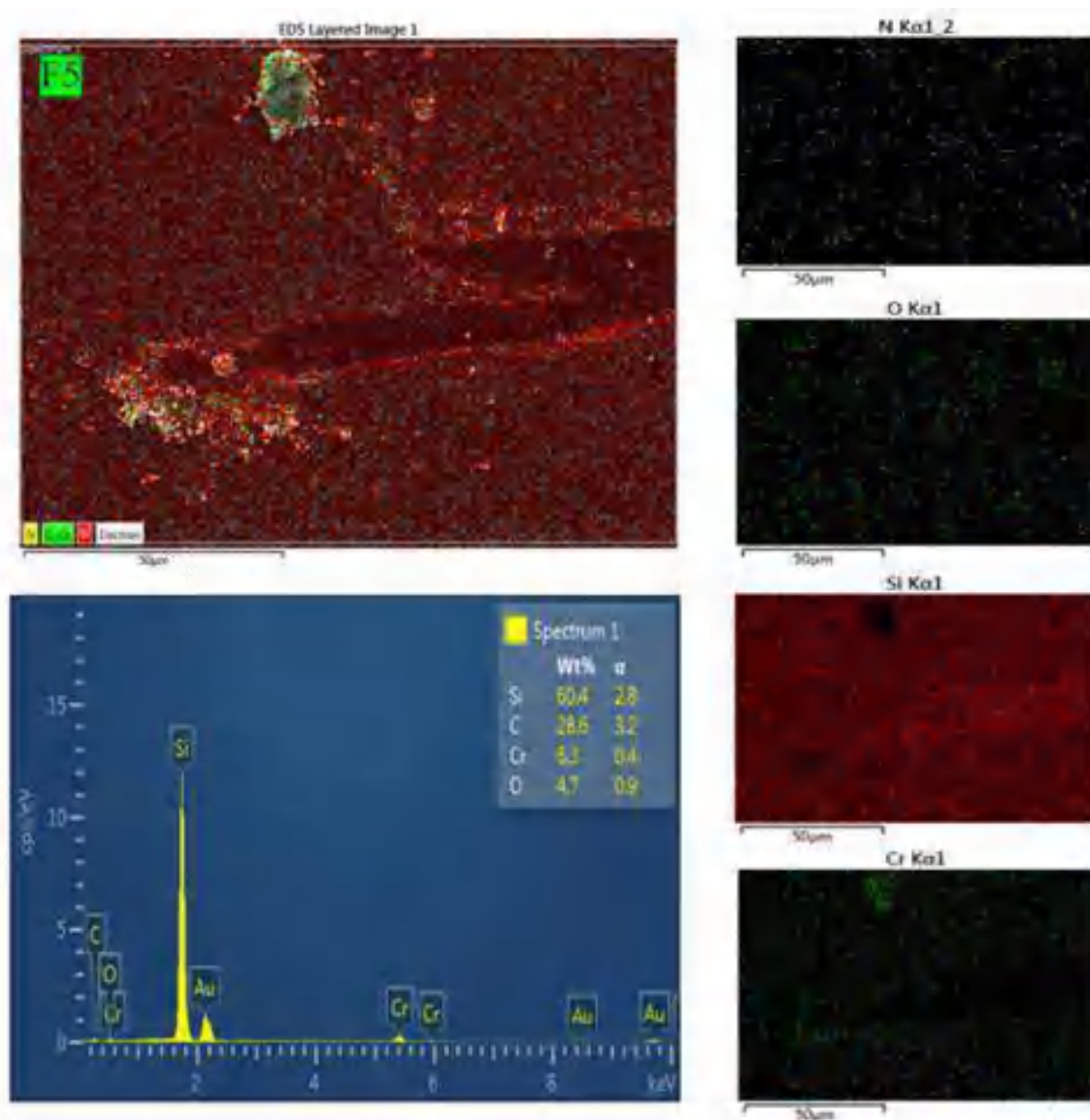


Figure 27: Cross-section EDS of the layered image of sample F5

3.2.5 Optoelectronic Study

(a) Bandgap

A JASCO-V670 spectrophotometer was used to evaluate the film's optical properties. As a result, optical transmission data across a large wavelength range (200 nm to 2000 nm) could be acquired. The transmitted data obtained is processed to calculate other optical relations such as the refractive index, loss factor, optical conductivity, dielectric constants, and skin depth necessary to evaluate

details regarding the electrical structure and possible use of CrN and CrN_xO_{1-x} films in optoelectronic applications.

The analysis of the optical spectra of the film was acquired. Report from the literature affirms that CrN is an indirect band gap semiconductor, and hence its power of transition in the equation below takes the power of half. The optical band gap of the films is computed using Tauc's relation [93] related as:

$$(\alpha h\nu)^{1/2} = \delta(h\nu - E_g)$$

where $h\nu$ is the incident photon energy, α is the absorption coefficient obtained by the relation defined as $\frac{2-\log(T)}{d}$, where T and d are the transmittance and thickness of the films respectively, and δ is the constant of proportionality. The bandgap is obtained from the extrapolation of the linear line fitting of the horizontal x-axis of the $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot when the vertical y-axis of the of the $(\alpha h\nu)^{1/2} = 0$.

The bandgaps for the grown films F1 to F3* are 0.27 eV, 1.63 eV, 2.49 eV, 2.60 eV, 2.65 eV, 2.18 eV, 3.63 V, and 2.48 eV respectively. The obtained bandgap is also presented in Table 2. As the nitrogen flow rate and oxygen incorporation increase during the growth process, the bandgap energy exhibits an increasing value which eventually decreases at a higher nitrogen flow rate due to the reduced free mean path caused by high nitrogen flow. The CrN thin films produced by reactive magnetron sputtering and in a report of publication by Gall et al. [94] established that the bandgap of the F1 film is quite smaller than the stated value of pure Cr film. The bandgap of F7 matches the published value of 3.6 eV for Cr₂O₃ by [95], indicating that large amounts of oxygen have formed the Cr₂O₃ compound in the film. The higher bandgaps of F2, F3, F4, F5, F6, and F3* indicate that residual oxygen gas in the growth chamber has been incorporated into the films. It is confirmed from samples F3 and F3* that variation in the deposition rate plays an insignificant role in the bandgap values of the films.

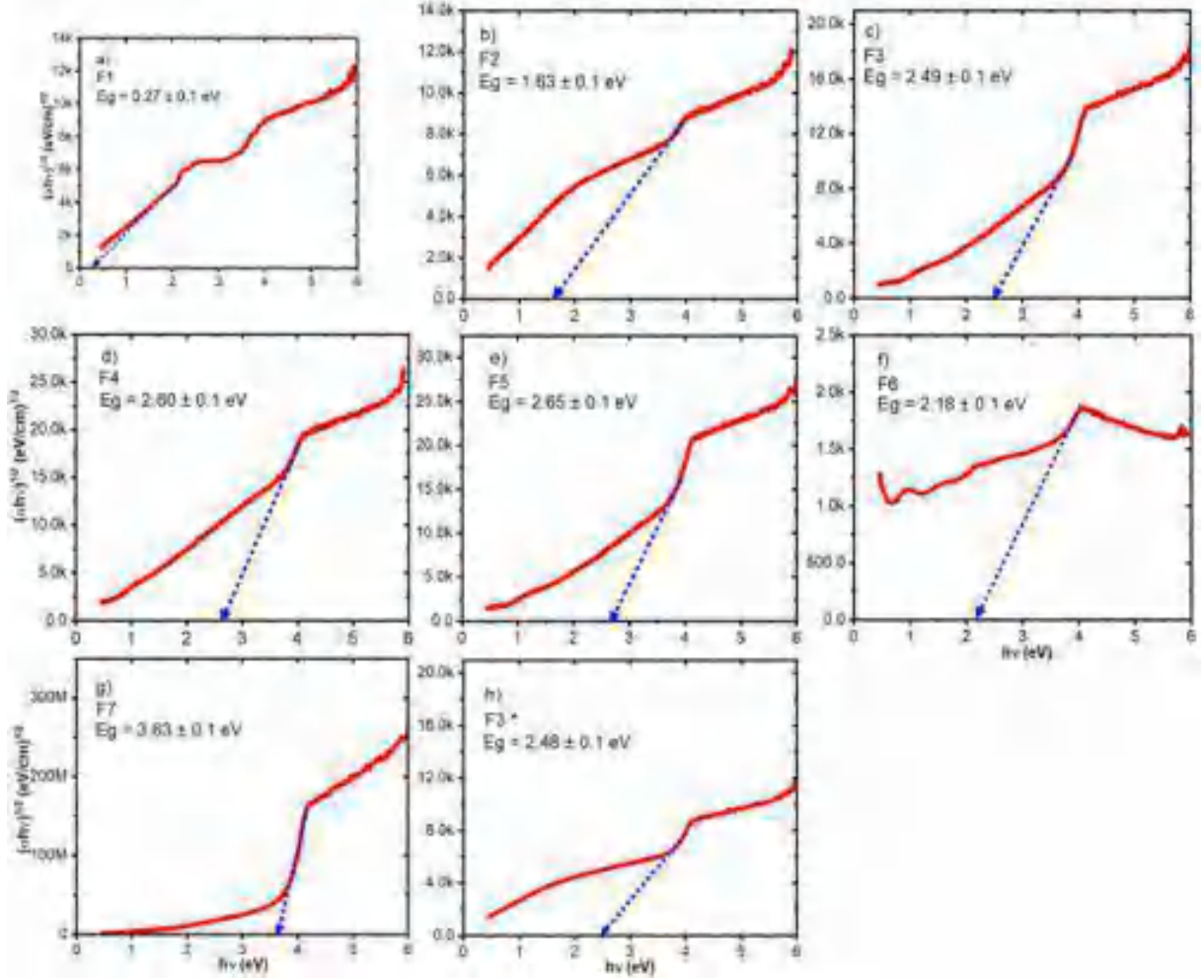


Figure 28: Tauc plot of CrN/glass of F1, F2, F3, F4, F5, F6, F7 and F3* thin films

The bandgap dependency on the reactive gas flow rate ratio is presented in Figure 29 below. The changes to the bandgap is due to the variation of the nitrogen flow rate incorporation in the RF magnetron sputtering chamber. These obtained results implied that the films require short radiation wavelengths for photovoltaic conversion, demonstrated an efficient and good performance of the cell, efficient absorption of sunlight, durability, potential for tandem cell, minimized thermal losses, and good resistance to degradation. Other obtained optoelectronic results highlight the potential of the film for energy harvesting as well.

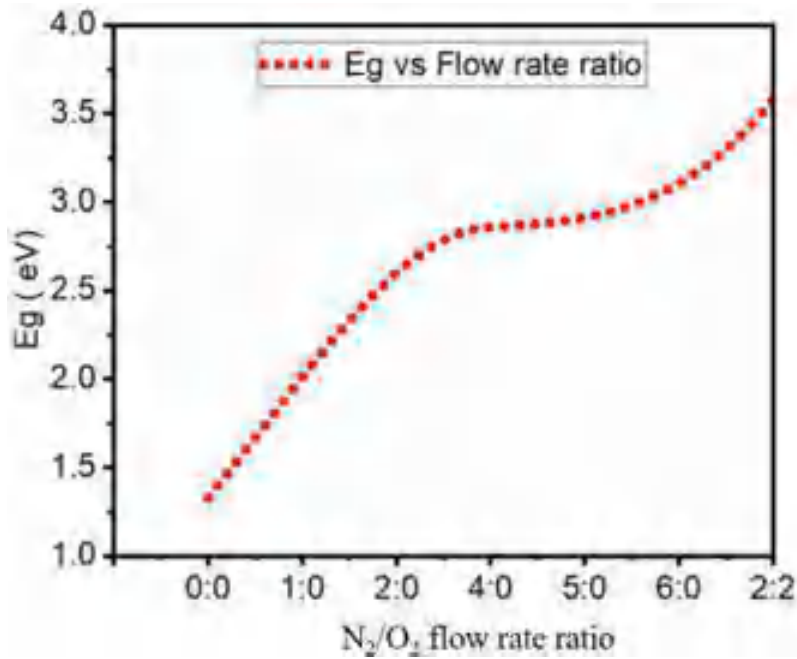


Figure 29: Energy band gap on the flow rate ratio

(b) Extinction Coefficient

The extinction coefficient is a property that describes how effectively a species behaves towards an incident beam of light or radiation such as absorbance or reflectance (scattering) mechanism at certain wavelengths. scattering mechanisms. It is expressed as $k = \frac{\alpha \lambda}{t}$, where α is the absorption and t is the sample thickness. The extinction coefficient of the samples is shown in Figure 30. This determines or confirms the capability of the film toward the efficient absorption of photons from sunlight. The lower extinction values represent the surface smoothness of the film and the lower loss of light energy by scattering and absorption.

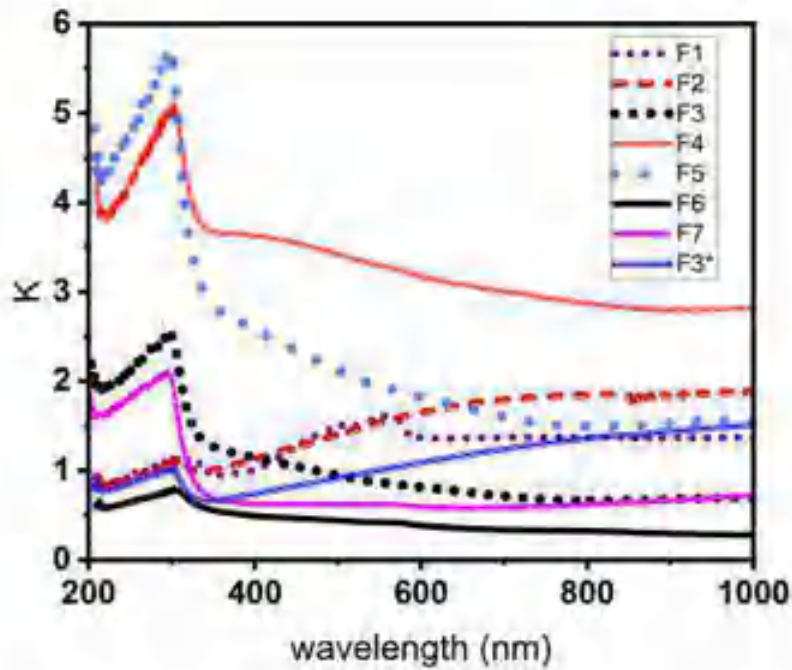


Figure 30: Extinction coefficient of the thin films

(c) Dielectric Constants, Loss Factor, and Optical Conductivity

Other optical properties parameters such as the real dielectric constant, imaginary dielectric constant, loss factor, and optical conductivity of the film variations with the wavelength and nitrogen flow rate are depicted in the figure below.

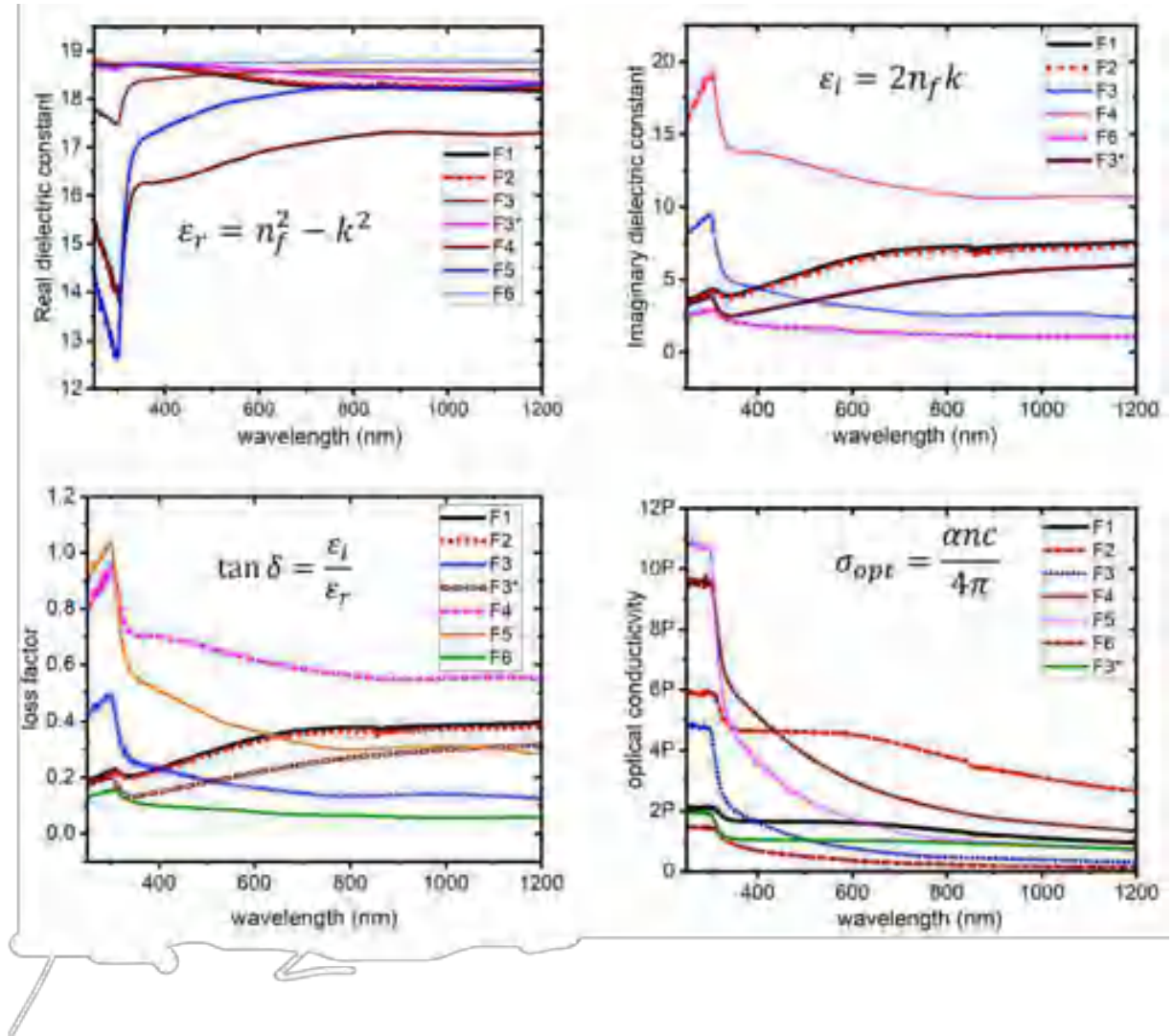


Figure 31: Film dielectric constants, loss factor, and optical conductivity

Owing to the different growth parameters of the film, the peaks of the prepared film showed a decrease sharply in the ultraviolet region and static or constant visible region and beyond. The real dielectric constant related to the dispersion of traveling light decreases the speed at which light waves propagate through that material, whereas the imaginary dielectric constant oversees absorbing energy from the electric field because of dipole movement, hence quantifying the disruptive rate of the wave in the film. The higher loss factor in the film is associated with the lower imaginary dielectric constant. The increase in the optical conductivity of the film could be ascribed to the rising of the absorption coefficient (α). The optical conductivity is most intense at

a lower wavelength of light because the light with a smaller wavelength represents increased photon energy, which facilitates electron transport.

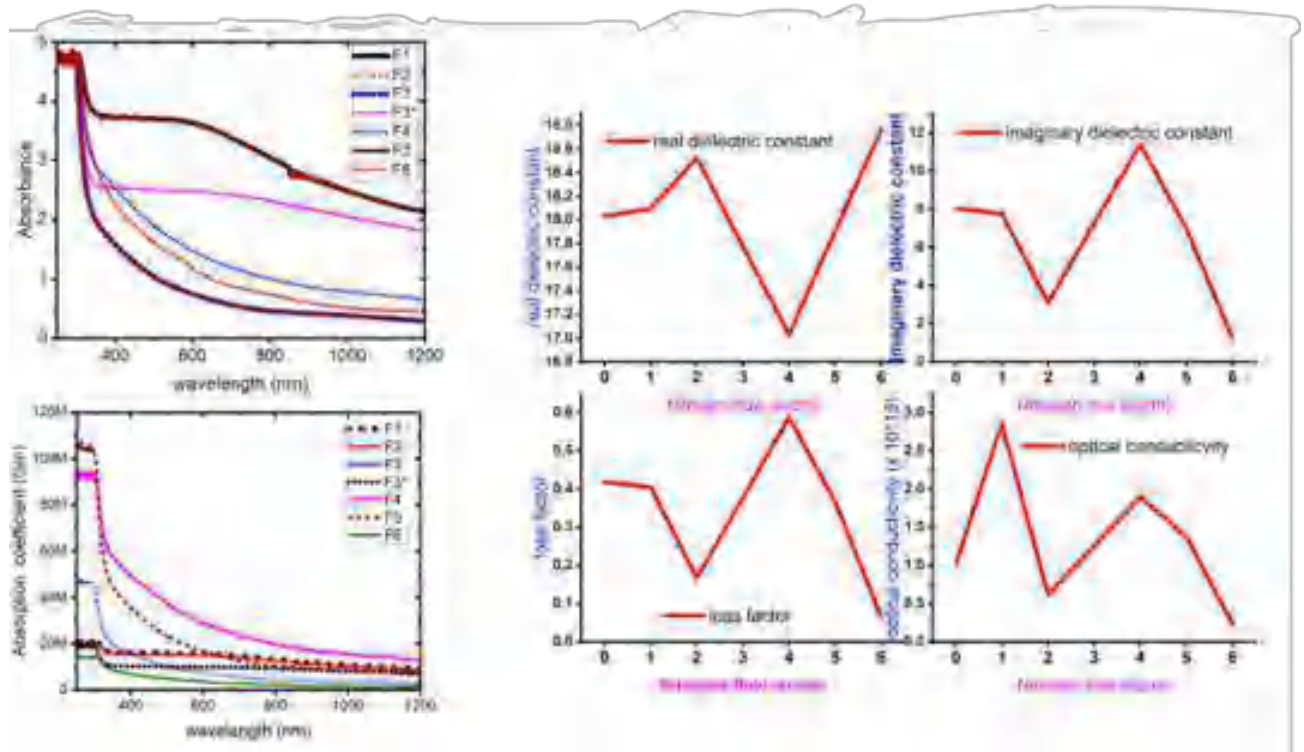


Figure 32: film absorbance, absorption coefficient, and nitrogen flow rate influence on the optoelectronic parameters

The absorbance spectra for the same range of light, absorption coefficient and variation of the dielectric constants, loss factor, and the optical conductivity influence on the nitrogen flow rate are depicted in the figure above. The behavior as a semiconductor has been confirmed by the observation of an absorption edge localized between 300 and 400 nm, which matches the excitonic bandgap of films [96]. There is no regular pattern of nitrogen flow rate on the optical properties due to other factors that could account for variation to the properties such as changes in the processing gas and chamber pressure, and radiofrequency power.

(d) Transmittance and Reflectance

The transmittance and reflectance of the films is shown in the figure below. The film demonstrated different behaviors toward the transmitted and reflected light. The films demonstrated low transmission towards photon light and high reflectance.

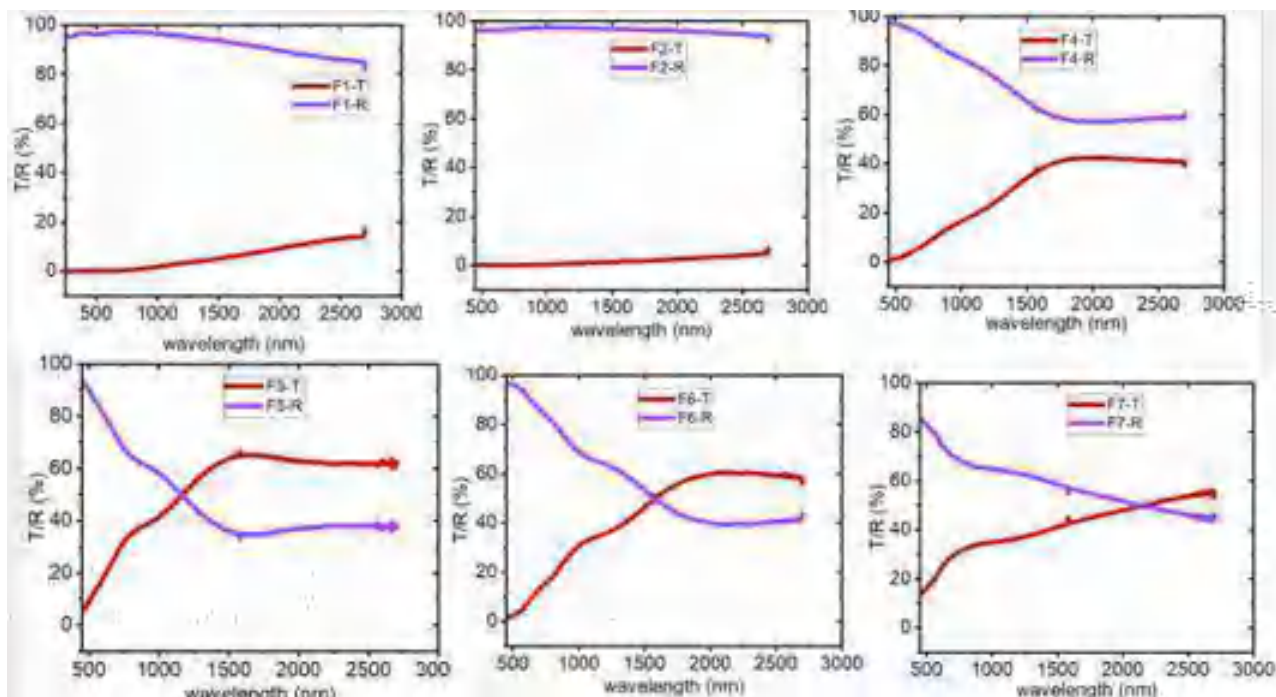


Figure 33: Transmittance and Reflectance

3.2.6 XPS Data Processing, Fitting, Etching, and Depth Profiling Study

(α) Data processing and fitting

X-ray photoelectron spectroscopy measurements were performed by ESCALAB 200-x spectrometer with an un-monochromatized Al K α radiation. The analysis of the data is done using Avantage software by applying Shirley background subtraction and employing Gaussian-Lorentzian peak fitting methods. This detailed chemical analysis helped in identifying the presence of Cr, N, and O species, and their chemical states, crucial for understanding the film's stoichiometry and purity. Different single peaks were added to the background and satellite contributions to fit the curves and the resulting data was compared to the raw data sets. The degree of fitting was assessed by Normal chi-square, Powell fitting algorithm, and the product of the Gaussian/Lorentz max ratio. After background removal using the Smart approach, experimental XPS spectra were deconvoluted utilizing well-characterized reference experimental carbon spectra for a specific contributing species. Peak location, height, width, and the Gaussian/Lorentzian ratio which are the unique properties of these reference peaks, were maintained throughout the deconvolution process. Before deconvolution, the survey ID automatically identifies the spectrum survey while the charge shift corrects the energy scale of the apparent charging. Following the film

growth procedure, samples exposed to air while setting for the XPS characterization caused the oxidization of the film. As a result of this, Oxygen peaks are observed in samples grown with and without oxygen flow concentration. The analyzed survey of the film confirms the presence of Cr, N, and O species as well as contamination from C and Si. After a thorough analysis, the peak positions, and intensities of the peaks of the different species of chromium Cr 2p, nitrogen N 1s, oxygen O 1s, and carbon C 1s were identified. The appearance of the C1s peak was caused by organic contamination of the sample after exposure to the atmosphere, while 284.6 eV of the binding energy of C1s was used as a reference peak to adjust the data for any shift in the spectrum caused by any charging effect. The survey ID of the peaks for the Unetched, etched, and depth profile analysis are shown in Figure 34 below.

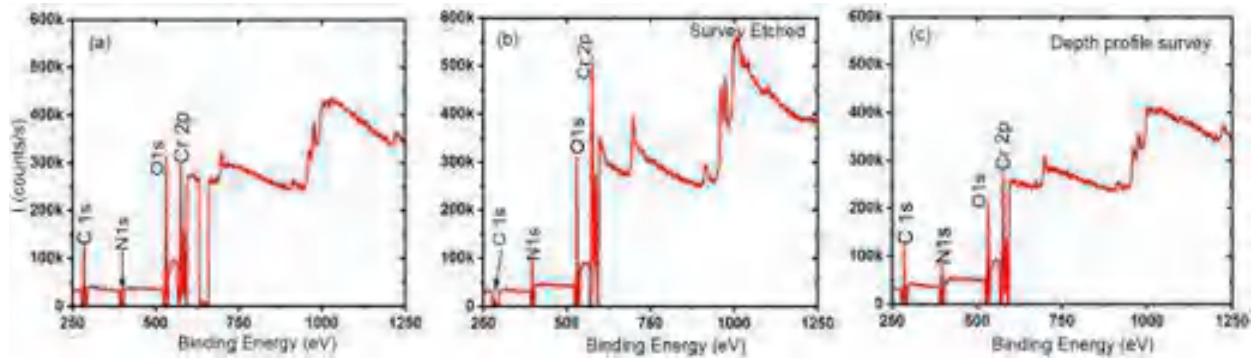


Figure 34: Full scan XPS survey of Unetched, etched, and depth profiles of the thin films

The spin-orbit coupling causes the Cr 2p spectrum to be split into the Cr 2p_{3/2} and Cr 2p_{1/2} peaks. The samples Cr 2p_{3/2} and Cr 2p_{1/2} peaks of the high-resolution spectra are deconvolved into four peaks that correspond to Chromium in oxide/hydroxides state (Cr₂O₃, CrO(OH), Cr(OH)₃; 576.7±0.2 eV [97,98], chromium in nitride-state (CrN_xO_{x-1}, CrN, Cr₂N; 574.90±0.5 eV [99,100] chromium in metallic-state (Cr⁰; 573.9±0.2 eV [101], and higher valency specie of chromium (Cr^{VI} 578.8±0.2 eV [102]. The chemical state and oxidation state of the different deconvoluted chromium peak and binding energy of the Cr2p_{1/2} orbit are named in corresponding to the Cr2p_{3/2} orbit with an approximate energy difference of $\Delta E = 9.4$ eV. An increment in the metallic chromium state is observed on the samples with no and low flow of nitrogen with a binding energy of 583.03±0.2 eV in Cr 2p_{1/2} peaks of sample F1 and 573.9 eV±0.2 eV and 583.1±0.2 eV binding energy in sample F2 Cr 2p_{3/2} and Cr 2p_{1/2} peaks

respectively. The chromium oxides of these samples are shifted to higher binding energy as well. The intensity of chromium in a nitrogen environment in chromium nitride (CrN), chromium (II) nitride (Cr₂N), and chromium oxynitride (CrN_xO_{1-x}) state of the F2 to F6 samples lies between 573.9±0.2 eV in the Cr 2p_{3/2} spin orbit. The latter spin coupling orbit was in agreement with Milosev et.al the energy difference of $\Delta E = 9.4$ eV [102] of the photoionization cross-section. The intensity of the Chromium in the nitrogen environment increases with the increasing nitrogen flow concentrations while the potential of the residual oxygen gas seemed to be reduced in the same order. The sample F7 grown with nitrogen and oxygen concentrations posed a higher intensity of the chromium in the oxidic or hydroxydic state in the Cr2p_{3/2} spin coupling and a lower intensity in the Cr2p_{1/2} spin coupling, unlike the rest of the samples. This gives an indication of the difference between the oxygen residual gas and the oxygen grown- in the samples. A higher oxidizing state of chromium from chromium (iii) to chromium (vi) Cr^{VI} was also observed in the sample.

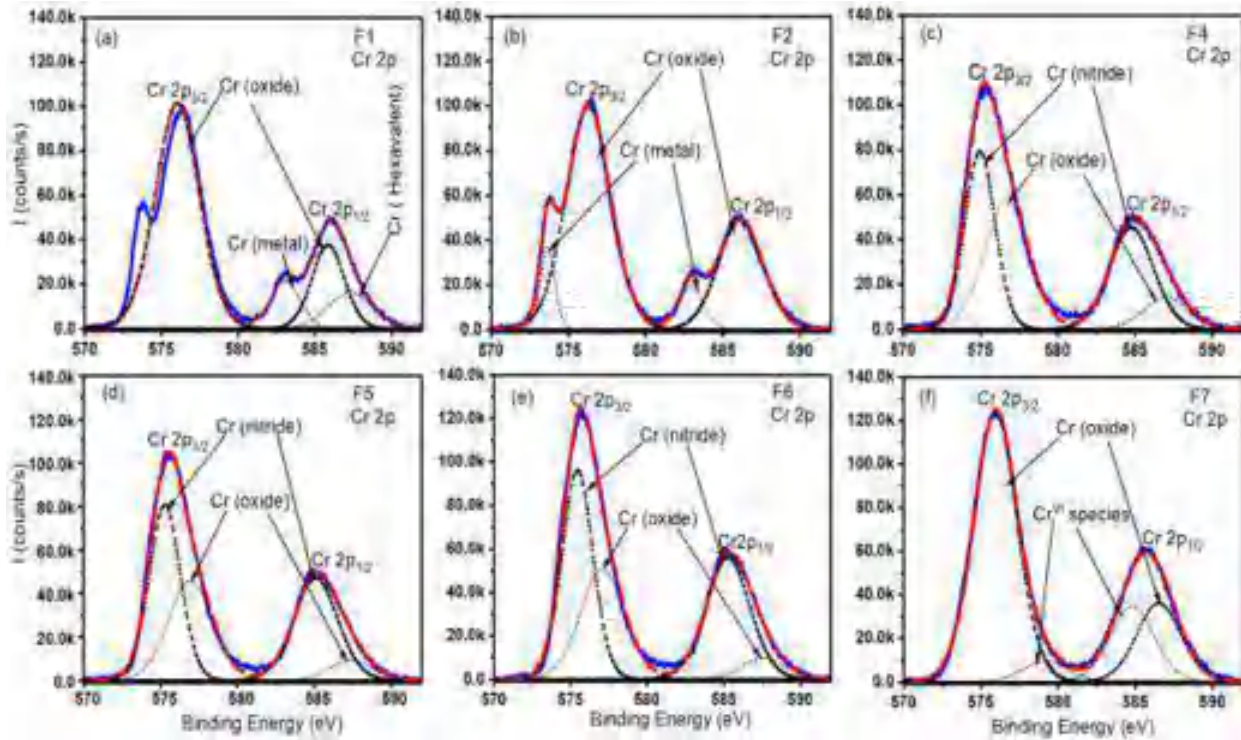


Figure 35: High-resolution XPS spectra of Cr2p of film F1, F2, F4, F5, F6, and F7

The N 1s species are shown in Figure 36. The peaks consist of three different kinds of peaks namely chromium nitride (CrN), chromium oxynitride (CrN_xO_y), and chromium nitrites/nitrates ($\text{Cr}(\text{NO}_3)_3$). The chromium nitride peaks were observed in all the samples grown with nitrogen concentrations with a binding energy of 396.9 ± 0.2 eV [100]. The intensity of this compound was found to be increasing fractionally with the increasing nitrogen flow concentrations. The chromium oxynitride (CrN_xO_y) peaks were also observed along with the Chromium peaks with the same regular pattern of growth conditions with a broad shoulder of 398.1 ± 0.2 eV binding energy. The CrN and ($\text{Cr}(\text{NO}_3)_3$) peaks with a binding energy of 399.0 ± 0.1 eV become lower in F7 because of nitrogen and oxygen uptake in the sample.

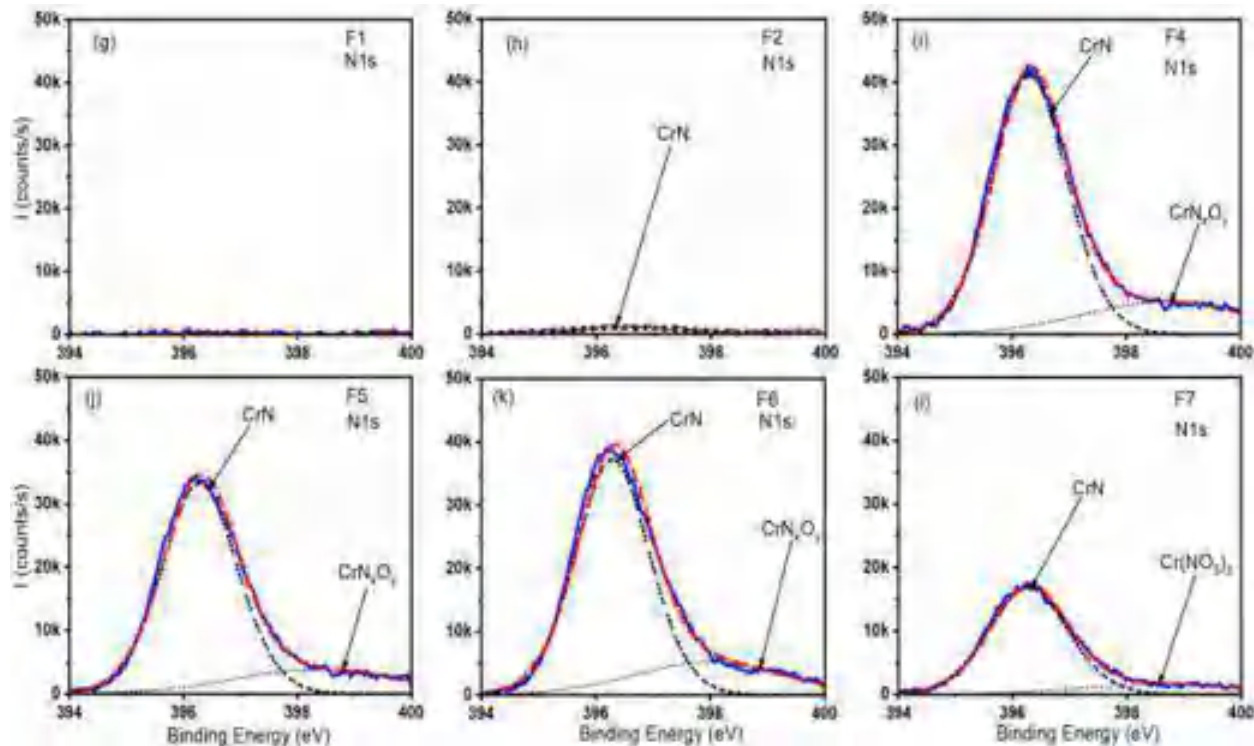


Figure 36: High-resolution XPS spectra of N 1s of film F1, F2, F4, F5, F6, and F7

Using peak fitting analysis, the O 1s species showed the presence of three different peaks namely; chromium oxide-state (Cr_2O_3 or CrO_3 ; 529.9 ± 0.2 eV) [103], chromium hydroxide state ($\text{Cr}(\text{OH})_3$ or $\text{CrO}(\text{OH})$; 531.5 ± 0.2 eV) [98], and organic compound species (533.2 ± 0.2 eV) [104] in all the samples as shown in Figure 37. The presence of the hydroxide species is due to the O–H from water molecules condensed on the film surface during deposition and the presence of residual gas

suggests that oxidation took place during air exposure while loading the substrates into the XPS chamber. The hydroxide peaks are observed on the sample grown with and without nitrogen concentration though an oxide and organic peaks are found in the sample grown with nitrogen or oxygen. It could be justified from the peak fitting analysis that the formation of the oxide species in samples F2, F4, and F7 is due to the low nitrogen concentration, and the organic species in samples F5 and F6 are due to high nitrogen concentration flow.

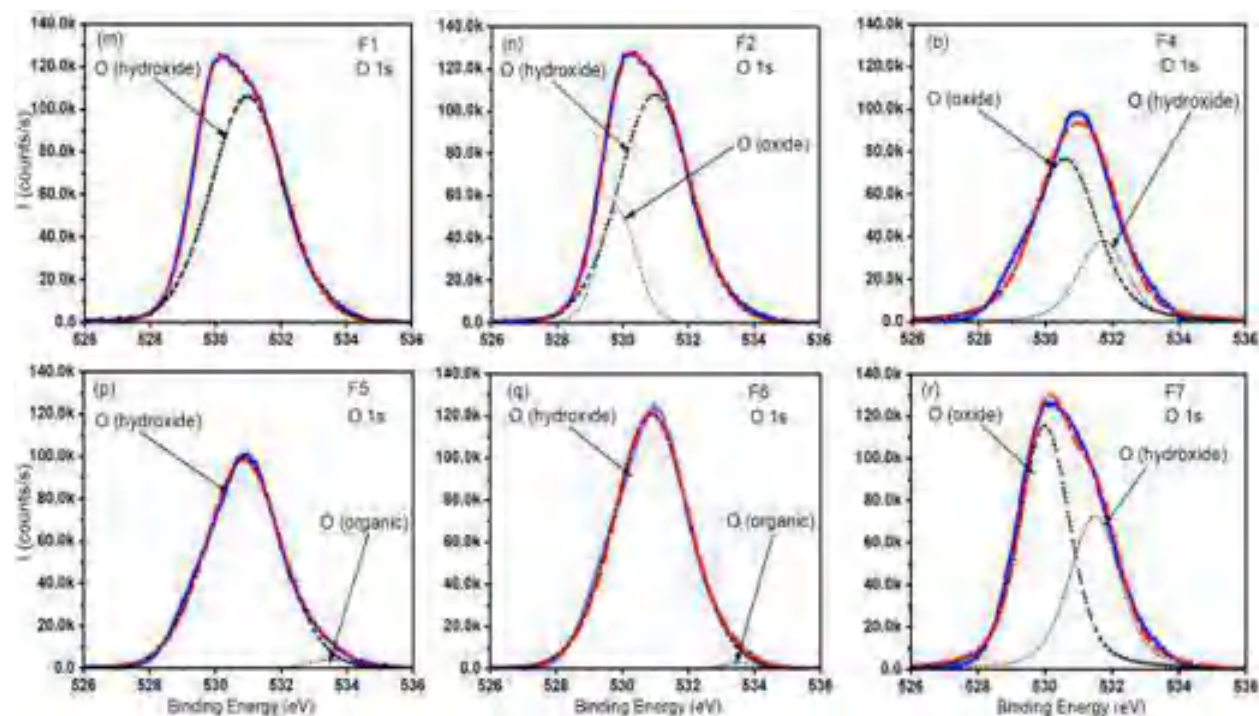


Figure 37: High-resolution XPS spectra of O 1s of film F1, F2, F4, F5, F6, and F7

The high-resolution XPS spectra of the etched samples are shown in the Figure 38. The same elements and compounds were found in the other analysis but varied in the intensity of the elements or compounds.

(β) Etching

The selected samples underwent etching to remove the oxide interference on the surface. The figure below represents the result obtained from the process.

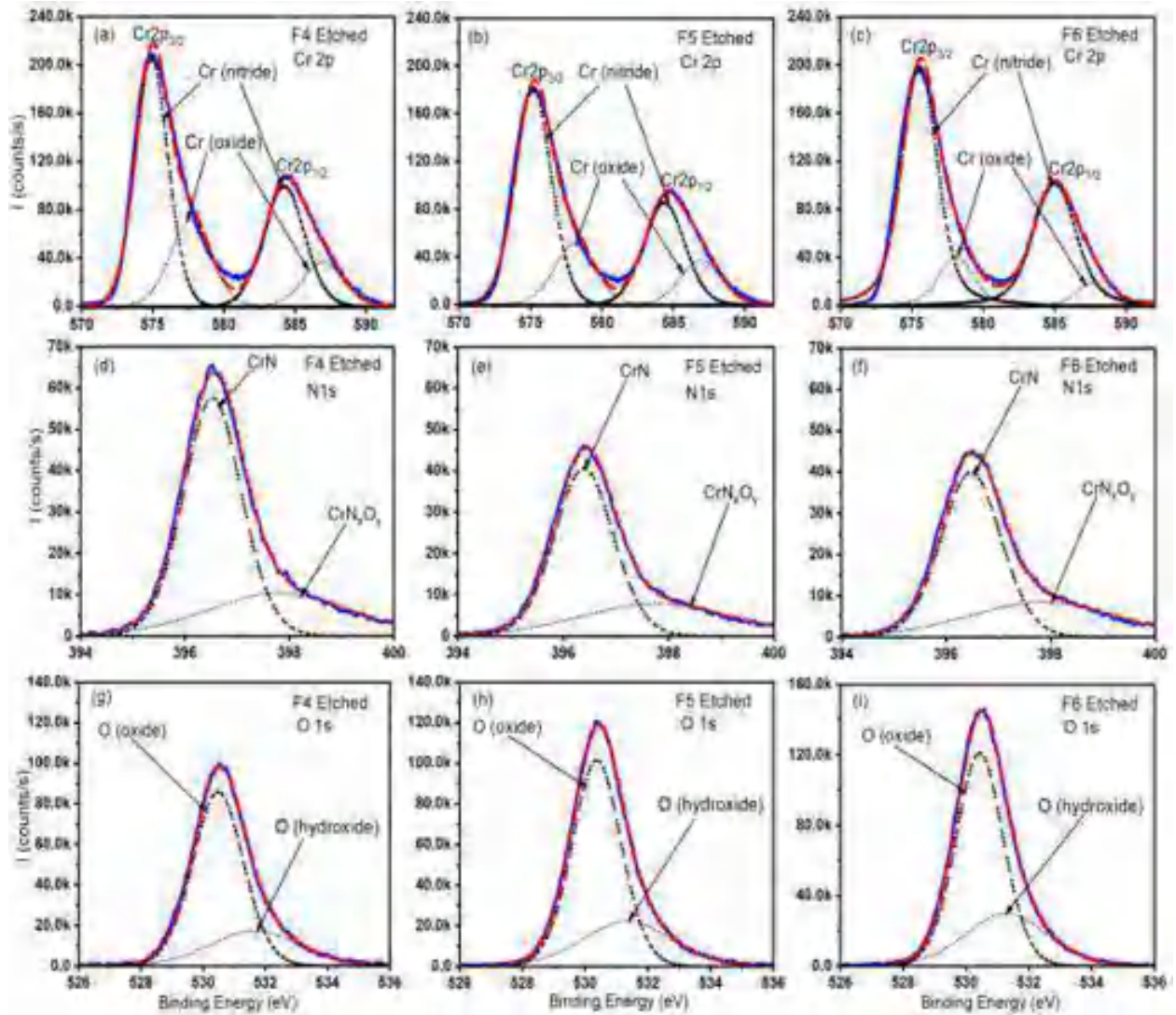


Figure 38: High-resolution XPS spectra of the etched thin films

(γ) Depth Profiling

Depth profiling of the high-resolution XPS spectra is shown in the Figure 39. The same element and compound were found in the other analysis but varied in the intensity of the element/compound.

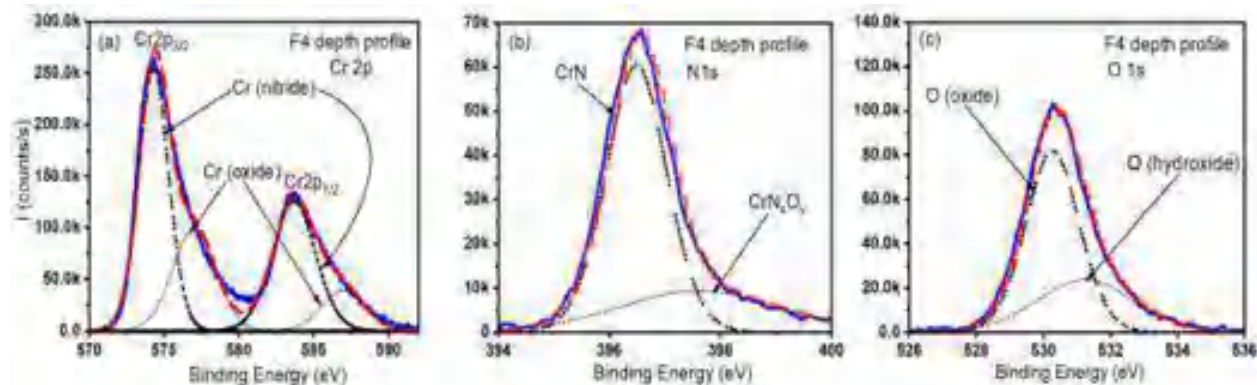


Figure 39: High-resolution XPS spectra of the depth profile thin films

The combined high-resolution comparison spectra of the unetched, etched, and depth profiles of sample F4 are shown in Figure 39. The intensity of the Cr 2p_{3/2} and Cr 2p_{1/2} peaks increases as the samples are etched and depth profiled, shifting the Cr (nitride) peaks to fractionally higher binding energy. The Cr 2p of the Cr (oxide) poses no difference in the intensity and binding energy of the sample. The intensity of the N 1s spectra of the CrN and O 1s of the (oxide) peaks increases as the samples are etched, depth profiled, and centered at 396.48 ± 0.2 eV and 530.43 ± 0.2 eV respectively, Chromium oxynitride gets broader while the hydroxide peak is low when etched.

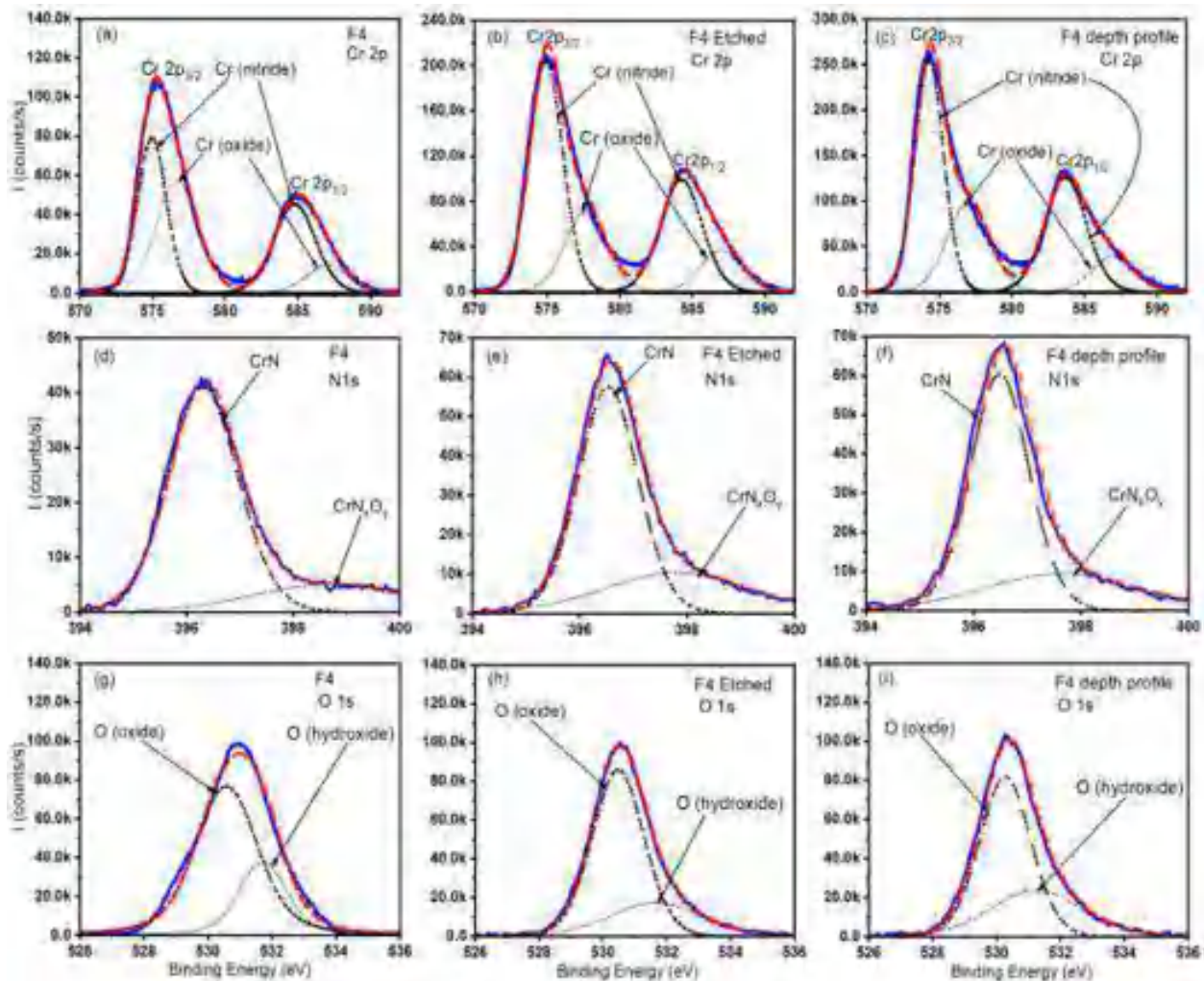


Figure 40: High-resolution XPS spectra of the Cr 2p, N 1s, and O 1s of the unetched, etched, and depth profile of the F4 thin film

The XPS of the Cr 2p, N 1s, and O 1s species peak binding energy, full width at half maxima, area, and the percentage atoms of the films before and after etching are provided in the tables below. The results show different variations in values of the parameters and this is ascribed to the growth parameters influence on the film.

Table 4: XPS of Cr 2p peak binding energy, FWHM, area, and % atom of thin films

	films	Binding energy (eV)		FWHM (eV)		Area (cps) x10 ⁶		% atom	
			etched		etched				etched
Cr 2p	F1	575.70	574.47	4.63	4.58	1.70	3.86	17.21	40.99
	F2	575.63	574.7	4.62	4.65	1.71	3.98	17.22	41.42
	F4	576.01	574.73	4.01	4.48	1.70	3.97	15.55	39.13
	F5	576.20	575.02	3.91	4.42	1.80	3.59	16.69	37.92
	F6	576.32	575.26	3.89	4.34	1.88	3.90	16.46	38.01
	F7	576.40	577.85	4.09	3.26	2.03	2.50	18.43	38.62

Table 5: XPS of N 1s peak binding energy, FWHM, area, and % atom of thin films

	films	Binding energy (eV)		FWHM (eV)		Area (cps) x10 ⁶		% atom	
			etched		etched		etched		etched
N 1s	F1								
	F2	396.5	396.69	2.59	2.00	0.29	0.41	0.62	0.64
	F4	396.01	396.14	2.87	2.85	0.26	0.36	15.05	22.46
	F5	396.96	396.16	2.92	2.91	0.23	0.28	13.65	18.95
	F6	397.02	396.22	2.89	2.91	0.25	0.28	13.97	17.60
	F7	396.98	396.99	2.92	2.92	0.11	0.04	6.55	16.94

Table 6: XPS of O 1s peak binding energy, FWHM, area, and % atom of thin films

	films	Binding energy (eV)		FWHM (eV)		Area (cps) x10 ⁶		% atom	
			etched		etched		etched		etched
O 1s	F1	530.19	529.98	3.41	2.9	1.10	1.09	42.84	46.09
	F2	530.13	529.99	3.34	2.89	1.08	1.06	43.27	43.98
	F4	531.20	530.04	3.53	3.14	0.89	0.70	32.32	27.39
	F5	531.21	530.06	3.38	3.07	0.86	0.82	32.76	34.55
	F6	531.27	530.15	3.36	3.00	1.02	0.93	35.68	36.22
	F7	531.03	530.16	3.42	3.18	1.10	0.15	39.78	38.01

Table 7: XPS of C 1s peak binding energy, FWHM, area, and % atom of thin films

	films	Binding energy (eV)		FWHM (eV)		Area (cps) x10 ⁶		% atom	
			etched		etched		etched		etched
C 1s	F1	284.20	284.19	2.67	3.34	0.39	0.10	39.96	10.69
	F2	284.15	284.25	2.76	3.79	0.39	0.12	39.51	12.95
	F4	284.95	284.06	2.84	4.82	0.40	0.10	37.07	10.07
	F5	285.00	284.27	2.79	4.36	0.39	0.07	36.88	7.59
	F6	285.07	284.29	2.86	3.49	0.38	0.07	33.83	7.06
	F7	285.08	284.56	2.73	1.33	0.37	0.09	33.90	7.04

Furthermore, as illustrated in Figure 30, the N/Cr ratio affects the B.E of the Cr2p and N1s peaks for CrN films that are formed by changing the nitrogen flow. When the nitrogen flow is 1, N/Cr =1, the B.E of Cr2p and N1s found were 575.53 eV and 396.93 eV, respectively. When compared to the growth parameter when nitrogen flow is 1, we discovered that the Cr B.E is distinctively decreasing, while the N1s B.E is distinctively increasing. This is evident that the Cr B.E decreases and in contrast, the B.E increases. The findings from the literature [104] affirmed that in the absence of ionization, the B.E of Cr 2p is 574.51 eV. This energy increases when Cr forms a bond with nitrogen; for example, when CrN is involved. Therefore, the B.E of Cr in CrN increases and takes on the value of 575.7 ± 0.4 while that of the N decreases. Another possible explanation for the stoichiometry changes, atomic structures, and packing densities is due to the different oxidation states of Cr ions and hybridization states.

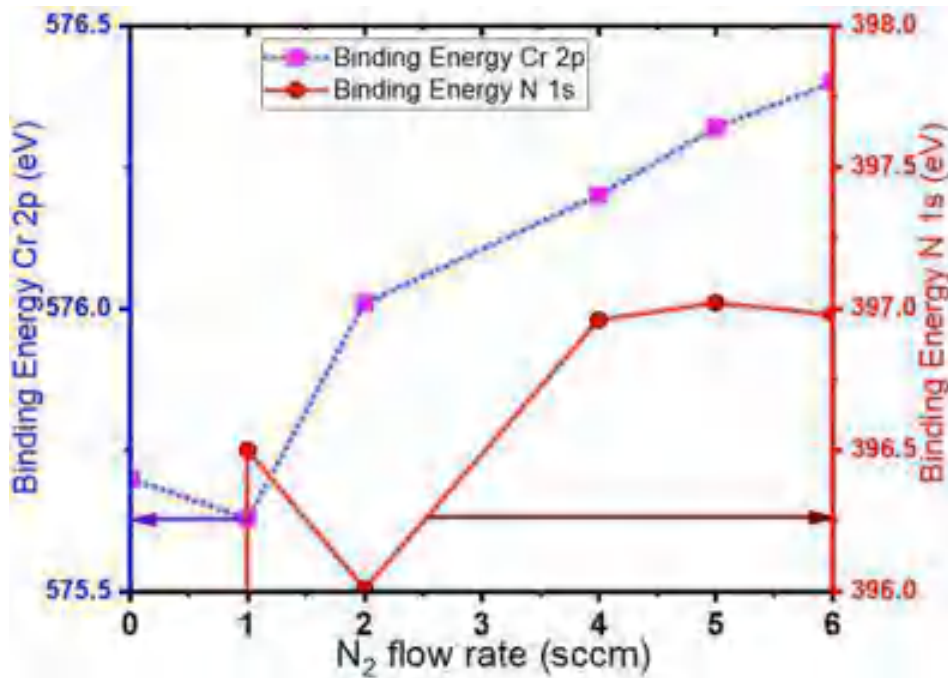


Figure 41: Binding energy of Cr and N depending on the N/Cr ratio

3.2.7 Hall Effect Analysis and Sheet Resistance Study

(a) Electrical Resistivity, Carrier Density, Mobility, Semiconductor Nature

A Lakeshore setup with an EM4-HVA electromagnet was used to conduct the Hall effect experiment. The system comprises an adjustable electromagnet that produces a magnetic field of 5.00 kG and offers a smooth field cycled between positive and negative values of the applied magnetic field. The Van der Pauw's method offers insights into the charge transport behavior of the films. The probes were positioned at the four corners of the films. The films were set up so that the magnetic field was parallel to the direction to normal of the film surface. During the experiment, the electromagnet was kept at room temperature by continuously flowing chilled water. The Hall coefficient, electrical resistivity, majority charge carrier concentration and mobility, semiconductor type, and other observed data of the Si(001) and glass are all listed in Tables.

Table 8: Electrical resistivity, Hall coefficient, charge carrier density, mobility, Hall resistance, and types of semiconductors of F1, F2, F3, F4, F6, and F7 thin films on Si(001)

Sample	ρ ($\Omega\cdot\text{cm}$)	R_H (cm^3/C)	Type	n_H (cm^{-3})	μ ($\text{cm}^2/\text{V}\cdot\text{s}$)
F1	1.0×10^{-2}	-1.1×10^{-1}	n-type	3.7×10^{19}	-1.5×10^1
F2	3.1×10^{-3}	-5.8×10^{-1}	n-type	1.1×10^{19}	-1.9×10^2
F3	2.1×10^{-2}	-6.7×10^{-3}	n-type	6.1×10^{19}	-3.2×10^{-1}
F4	3.5×10^{-1}	1.3×10^2	p-type	6.2×10^{16}	3.5×10^2
F6	2.2×10^{-2}	1.1×10^1	p-type	2.4×10^{18}	5.4×10^2
F7	4.9×10^{-3}	2.0×10^1	p-type	6.5×10^{15}	1.9×10^2

Table 9: Electrical resistivity, Hall coefficient, charge carrier density, mobility, Hall resistance, and types of semiconductors of F1, F2, F3, F4, F6, and F7 thin films on fused silica substrates

films	ρ ($\Omega\cdot\text{cm}$)	R_H (cm^3/C)	Type	n_H (cm^{-3})	μ ($\text{cm}^2/\text{V}\cdot\text{s}$)
F1	1.5×10^{-2}	7.4×10^{-4}	p-type	5.2×10^{19}	7.0×10^{-1}
F2	6.8×10^{-3}	1.2×10^{-4}	p-type	1.2×10^{22}	1.8×10^{-2}
F3	2.4×10^{-2}	-1.1×10^{-3}	n-type	5.7×10^{19}	-4.7×10^{-2}
F4	4.2×10^{-2}	-1.5×10^0	n-type	1.5×10^{14}	-1.5×10^1
F6	1.5×10^{-1}	3.1×10^2	p-type	1.9×10^{16}	1.5×10^3
F7	1.7×10^{-2}	-3.1×10^2	n-type	2.2×10^{16}	-2.1×10^3

Table 10: Hall resistance of the Si(001) substrate of F1, F2, F3, F4, F6, and F7 thin films

films	$R_{ab}(\Omega)$	$R_{bc}(\Omega)$	$R_{cd}(\Omega)$	$R_{da}(\Omega)$	$R_{ac}(\Omega)$	$R_{ca}(\Omega)$
F1	-4.0×10^1	-4.8×10^1	-4.1×10^1	-4.8×10^1	7.5×10^0	7.5×10^0
F2	-1.4×10^1	-1.4×10^1	-1.4×10^1	-1.4×10^1	-7.1×10^1	-7.1×10^1
F3	-8.3×10^1	-1.0×10^2	-8.3×10^1	-1.0×10^2	1.9×10^1	1.9×10^1
F4	-3.0×10^3	-7.6×10^2	-3.1×10^3	-5.7×10^2	-2.4×10^3	-2.4×10^3
F6	-4.1×10^1	-1.5×10^2	-2.1×10^2	-4.8×10^1	-3.8×10^1	-1.8×10^1
F7	2.0×10^1	1.5×10^3	-1.1×10^2	1.3×10^3	7.7×10^2	-6.0×10^1

Table 11: Hall resistance of the fused silica substrate of F1, F2, F, F4, F6, and F7 thin films

films	$R_{ab}(\Omega)$	$R_{bc}(\Omega)$	$R_{cd}(\Omega)$	$R_{da}(\Omega)$	$R_{ac}(\Omega)$	$R_{ca}(\Omega)$
F1	-1.4×10^2	-2.3×10^1	-1.4×10^2	-2.3×10^1	-1.2×10^2	-1.2×10^2
F2	-4.6×10^1	-1.9×10^1	-4.6×10^1	-1.9×10^1	-2.7×10^1	-2.7×10^1
F3	-1.1×10^2	-9.8×10^1	-1.1×10^2	-9.8×10^1	-1.3×10^1	-1.3×10^1
F4	-1.0×10^1	-1.0×10^3	-6.8×10^2	-1.5×10^1	8.6×10^0	6.6×10^0
F6	-1.4×10^2	-2.3×10^1	-1.4×10^2	-2.3×10^1	-1.2×10^2	-1.2×10^2
F7	-1.1×10^3	-4.0×10^2	9.5×10^1	-1.6×10^2	-2.4×10^2	2.2×10^2

The list of tables above showed the electrical resistivity (ρ), Hall coefficient (R_H), charge carrier density (n_H), mobility (μ), and types of the semiconductors in the ascending order of nitrogen flow rate. The highest mobility and charge carrier concentration of the n-type and p-type semiconductor thin films of a Si(001) as shown in Table 8 is $6.1 \times 10^{16} \text{ cm}^{-3}$ and $-3.2 \times 10^{-1} \text{ cm}^2/\text{V.s}$ respectively at highest nitrogen flow concentration of n-type in sample F3 whereas for the p-type semiconductor, the thin film F6 has the mobility of $2.4 \times 10^{18} \text{ cm}^{-3}$ and charge carrier density of $5.4 \times 10^2 \text{ cm}^2/\text{V.s}$ which is also for the sample with highest nitrogen concentration. Also, there is a progressive order of switching from n-type to p-type in the films based on the nitrogen flow rate. The lowest electrical resistivity of the n-type semiconductor film lies on the sample grown with 1sccm nitrogen concentration while the lowest electrical resistivity of the p-type semiconductor film lies on the sample grown with nitrogen and oxygen in the ratio 2:2 flow rate. In Table 9, the lowest electrical resistivity ($6.8 \times 10^{-3} \Omega.\text{cm}$) lies on the sample with a nitrogen flow rate of 1 sccm, and with the highest carrier density of $1.2 \times 10^{22} \text{ cm}^{-3}$. There is not a regular formalism observed in the switching between n-type and p-type semiconductor film on the fused silica substrate. The Hall resistance of the n-type semiconductor film is very small when compared to the p-type semiconductor film and the value ($5.8 \times 10^{-1} \text{ cm}^3/\text{C}$) is highest in the sample with lower nitrogen flow rate while the Hall resistance of the p-type semiconductor film is

highest in sample F7 with $2.0 \times 10^1 \text{ cm}^3/\text{C}$ for a Si(001) substrate. For a fused silica substrate, both the p-type and n-type semiconductor film have a relatively absolute same value of Hall resistance with $3.1 \times 10^2 \text{ cm}^3/\text{C}$, though the Hall resistances of the p-type are smaller in magnitude to the n-type semiconductor. Table 10 and Table 11 reveal the Hall resistances of the Si(001) and fused silica substrate respectively. The law reciprocity is valid for most of the resistance obtained in the measurements.

(b) Sheet Resistance

The sheet resistance (R_s) of the samples is shown in the Figure 42. It is obtained using the relation $R_s = \frac{\rho}{t}$. The sheet resistance is found to be increasing with the nitrogen flow rate until it reaches saturation and then begins to fall. It is highly dependent on the resistivity and the thickness of the sample, hence, the influence on the flow rate is ascertained based on the obtained figure below.

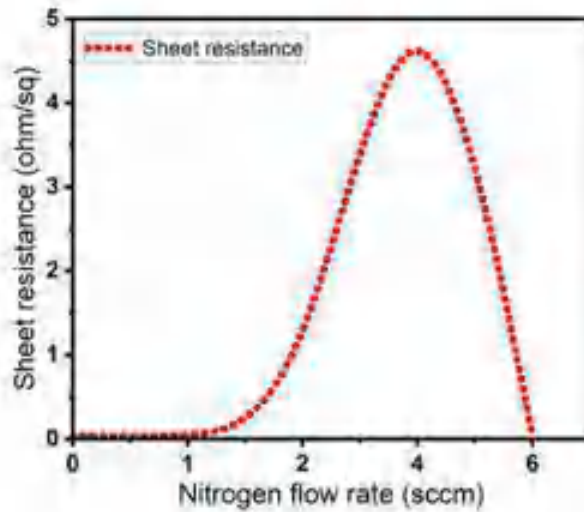


Figure 42: Sheet resistance of the thin films

3.2.8 Electrochemical Behavior Analysis

(1) Electrochemical Behavior Examination Approach

The investigation into the supercapacitive properties of the CrN thin films was meticulously executed using a CHI-760E electrochemical workstation, employing an array of electrochemical techniques to evaluate their performance as potential electrodes for supercapacitors. The

characterization encompassed cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy, each providing distinct insights into the electrochemical behavior of the films. The measurements were conducted in a symmetric two-electrode system, innovatively designed to assess the supercapacitive performance of the CrN films. The setup involved the use of CrN thin film-coated steel substrates as both the positive and negative electrodes, effectively forming a symmetric supercapacitor. A 1 mole H₂SO₄ aqueous solution was chosen as the electrolyte, known for its high ionic conductivity and compatibility with CrN materials. To prevent electrical contact between the electrodes while allowing ionic movement, a piece of filter paper was strategically placed between the two face-to-face CrN-coated electrodes, serving as an effective separator.

The specific capacitance (C_s) of the CV profile is derived using:

$$C_s = \frac{1}{A \times v \times \Delta V} \times \int I \times dV$$

where the area is $\int I dv$ in watt (w), v is the scan rate in v/s and Δv is the potential window in volt (v).

The specific capacitance (C_s) of the GCD profile is derived using:

$$C_s = \frac{I \times \Delta t}{A \times \Delta v}$$

where I is the discharging current (A), Δt is the discharging time in sec, a is the active area in cm², and Δv is the potential window in volt (v).

The energy density is calculated using:

$$E = \frac{5}{36} (C_s \times \Delta v^2)$$

The power density is calculated using:

$$P = 3600 \times \frac{E}{\Delta t}$$

Table 12: Electrochemical performance of film F1-based symmetric supercapacitor using CV measurement

Scan rate (mV/sec)	Area under the CV (mW)	Areal Capacitance (mF/cm ²)
20	2.6	65
40	4.7	59
60	6.6	55
80	8.3	52
100	9.9	50

Table 13: Electrochemical performance of film F1-based symmetric supercapacitor using GCD measurement

Current Density (mA/cm ²)	Areal Capacitance (mF/cm ²)	Energy Density (μ Wh/cm ²)	Power Density (μ W/cm ²)
0.5	75	10	250
1	59	8	500
2	55	8	1000
3	38	5	1500

(2) CV Result

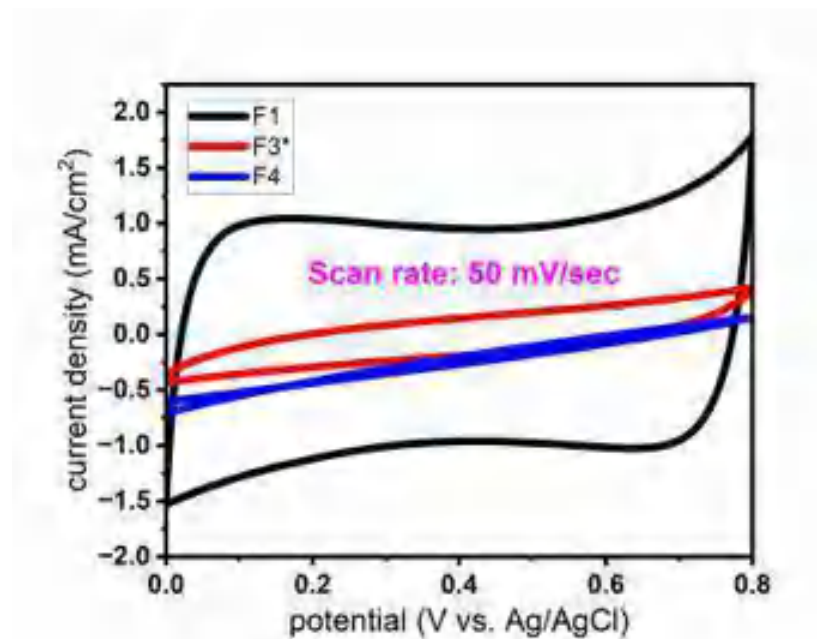


Figure 43: Comparison of CV curves for the F1, F3*, and F4 electrodes in 3 electrode electrochemical system, using 1 M H₂SO₄ electrolyte

The film CV curve, as seen in the above figure, is shaped like a symmetric rectangle of an electric double-layer capacitor (EDLC). This is because the film pores and increased open surface area facilitate the easier passage of ions through the film, resulting in a substantially higher current. This is significant because it demonstrates how the CrN-based film affects supercapacitance performance, as seen by the fact that the working electrode covered a greater area than the current collector. This is noteworthy because it shows that the CrN-based film plays a major role in supercapacitance performance. After all, the working electrode covered a larger area than the current collector. It is evident from this that the performance of the supercapacitance is significantly influenced by the CrN-based film. Ultimately, the area occupied by the active electrode was greater than that of the current collector. Utilizing a symmetric two-electrode arrangement and a 1 M H₂SO₄ aqueous electrolyte, CV was used to determine the electrochemical performance of the CrN thin films, namely F1, F2, and F4 at a scan rate of 50 mV/s. The results and findings obtained are shown in Figure 43.

Remarkably, the F1 film's cyclic voltammetry curve has a quasi-rectangular form, which is suggestive of the capacitive behavior typical of EDLCs. This form indicates that electrostatic charge buildup is most prevalent at electrode-electrolyte contact. The greater electroactive surface

area in the F1 sample is responsible for the noticeable current, and this is probably made possible by the surface pores and surface roughness of the film. The structural characteristics of the film facilitate ion mobility and improve charge storage capacity by making ions more accessible to the electrode surface. Figure 44, which shows the CV response of the F1 electrodes-based symmetric supercapacitor at different scan rates from 10 mV/s to 100 mV/s, offers more information about the capacitive characteristics of the films. Yet under conditions of rapid charging and discharging, as demonstrated by the film, the CrN films appear to retain good capacitive behavior, as evidenced by the retention of the symmetrical and reversible CV shape across a range of scan rates. With increasing scan rates, the peak current values rise due to the accelerated kinetics of ion transport [105]. However, the ability of the films to sustain their capacitive nature under such conditions underscores the resilience and efficacy of the film in supercapacitor applications. The electrochemical performance of the F1-based symmetric supercapacitor was quantitatively evaluated through the measurement of areal capacitance derived from the cyclic voltammetry profiles at different scan rates, using the equation above. The obtained result reveals a decline in capacitance with increasing scan rates. At the lower scan rate of 20 mV/s, the maximum areal capacitance reaches 65 mF/cm², signifying that the ions have ample time to interact fully with the electrode's surface. This interaction is a testament to the well-designed porosity and surface structure of the CrN films, which permit extensive ion penetration and interaction, leading to enhanced charge storage. As the scan rate increases, there is a consistent decrease in the specific capacitance, with a recorded minimum specific capacitance value of 50 mF/cm² at the highest rate of 100 mV/s. This observed trend is expected as higher scan rates offer less time for ions to diffuse into the electrode's pores, thus reducing the effective utilization of the available electroactive sites. The relationship between scan rate and capacitance is critical for supercapacitor configuration since it affects the capability rate of the device. The high capacitance values at lower scan rates are indicative of the potential for energy storage applications that require sustained energy release [106]. In contrast, the device's ability to maintain capacitance at higher scan rates positions it well for applications that demand rapid energy discharge, such as power buffering and load leveling in electronic circuits. The CV analysis elucidates the superior capacitive performance of the CrN thin films, with the F1 sample demonstrating particularly promising characteristics for supercapacitor electrodes. The films exhibit a balance of high areal capacitance and rate capability, essential for diverse energy storage applications. The supercapacitive behavior of the CrN thin

film, combined with their structural integrity and electrochemical stability, underscores their potential for advancing supercapacitor technology.

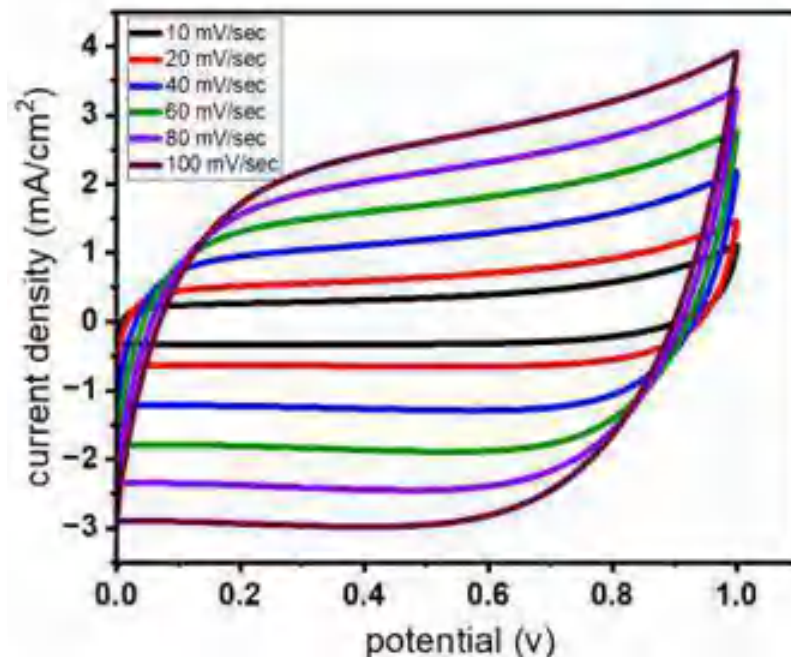


Figure 44: CV curves at different scan rates

The CV plot of the working electrodes of film F1 at various scan rates between 20 to 100 mV/s is shown in the figure above. The symmetric and reversible figure of the CV curves is an indication of good capacitive behavior.

(3) GCD Result

The GCD analysis is represented in the figure below. The GCD profiles of the CrN thin film supercapacitor is shown in Figure 45. The profiles were examined at multiple current densities between the current density of 0.5 to 3 mA/cm² in the potential window between 0 to 1.0 V. The CrN-based CrN supercapacitor electrode material exhibits typical charging (intercalation) and discharging (deintercalation) characteristics. It is distinctively unique by its substantially symmetric nonlinear triangular-based nature, which implies that the Faradic reaction and electric double-layer physisorption both aid the material ability to store energy, and by its relatively low voltage drop, which implies that the CrN thin films have a minimal equivalent series resistance.

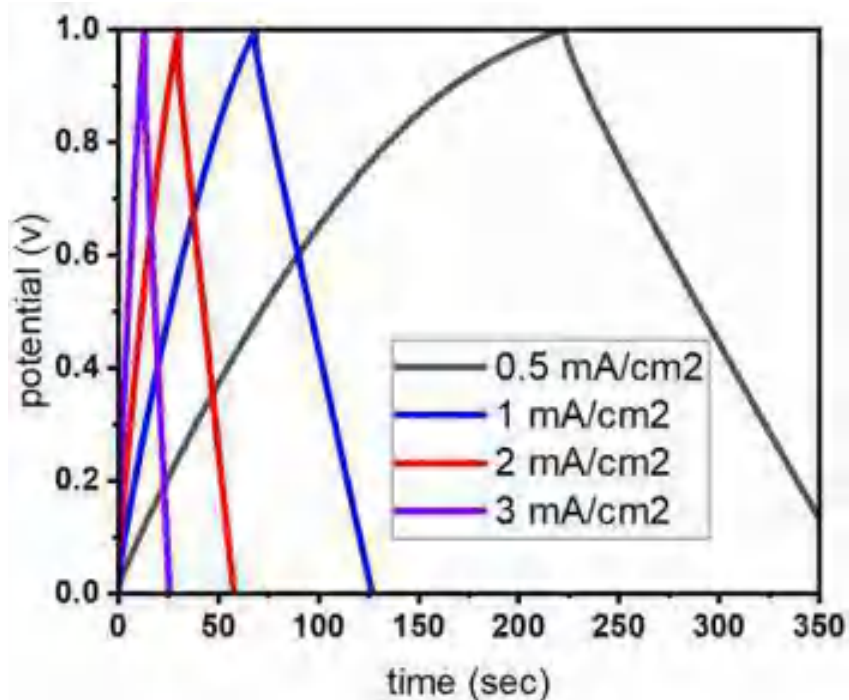


Figure 45: GCD profiles at different current densities

In particular, the electrochemical double layer is formed by the physisorption of hydrogen ions on surface active sites, whereas the Faradic process of hydrogen ion chemisorption takes place on the surface of CrN thin film electrodes. The electrochemical performance of CrN thin films as electrodes in symmetric supercapacitors has been extensively studied through GCD to understand their charge storage mechanisms and potential for energy applications. Figure 45 illustrates the GCD profiles at current densities ranging from 0.5 mA/cm² to 3 mA/cm² within a potential window of 0 to 1.0 V. The nearly symmetrical triangular shapes of the GCD curves underlined a balanced charge-discharge mechanism in the chronopotentiometry, suggesting both Faradic reactions and EDLC contribute to the energy storage mechanism [107]. This is further evidenced by the minimal voltage drop observed during the transition from charging to discharging, implying low internal resistance and efficient ion transport within the CrN films. The combined Faradic and double-layer processes, involving chemisorption and physisorption of electrolyte ions, respectively [108], on the CrN surface, resulted in an effective and stable charge storage system. The areal capacitance, as determined from both CV and GCD measurements, illustrates the dependence of capacitance on operational conditions. From CV analysis, as shown in Figure 46, the areal capacitance decreases from 65 mF/cm² at a 20 mV/s scan rate to 50 mF/cm² at a 100 mV/s scan rate. This

decrease aligns with the expected behavior where slower scan rates allow for more complete ion diffusion and interaction with the electrode surface, leading to higher capacitance values. Similarly, the GCD-derived capacitance depicted in Figure 46 also demonstrates a decline with increasing current density. The highest capacitance of 75 mF/cm² at 0.5 mA/cm² progressively decreases to 38 mF/cm² at 3 mA/cm². This trend can be attributed to the reduced ion intercalation efficiency at higher current densities, where the rapid charge-discharge cycles do not permit full utilization of the electrode's active material. The energy and power densities, critical parameters for supercapacitor performance, are represented in the Ragone plot as shown in Figure 47. The optimized F1 electrodes-based symmetric supercapacitor exhibits a maximum energy density of 10 μ Wh/cm² and a power density of 250 μ W/cm² at a current density of 0.5 mA/cm². As the current density increases to 3 mA/cm², the energy density decreases to 5 μ Wh/cm², whereas the power density increases to 1500 μ W/cm². This inverse relationship between energy and power density is characteristic of supercapacitors, where a trade-off is often observed, higher power outputs are achieved at the expense of energy storage capacity. The data from the GCD measurements for the F1-based CrN-based symmetric supercapacitor are detailed in Table 13. These results highlight the supercapacitor's capability to deliver varying levels of energy and power, rendering it appropriate for a variety of uses from long-term energy supply to rapid power bursts. The CrN thin film-based supercapacitors, with their high areal capacitance and favorable energy and power densities, present a promising avenue for the development of advanced energy storage systems.

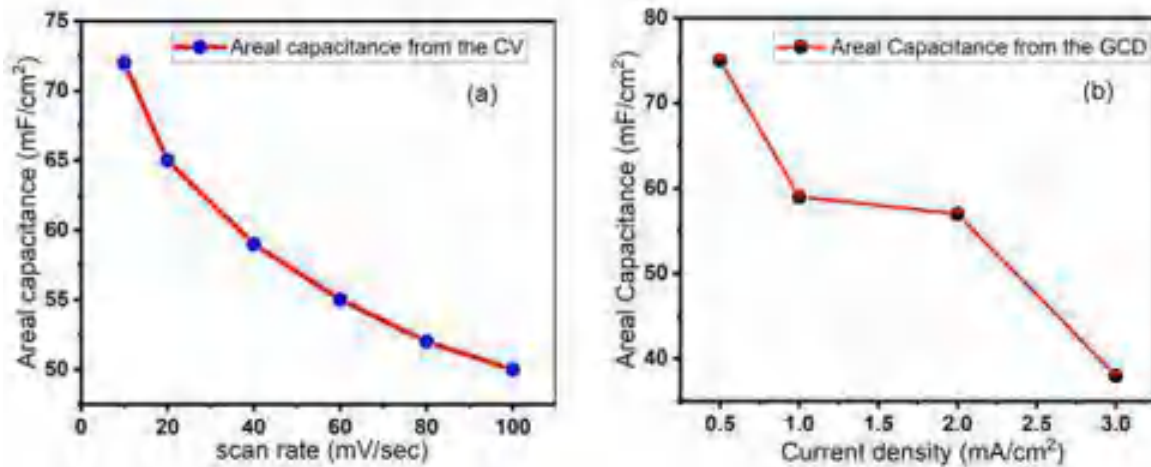


Figure 46: Areal capacitance from (a) CV and (b) GCD

The areal capacitances of the CrN-based F1 thin film symmetric supercapacitor derived from the cyclic voltammetry profiles at various scan rates and the galvanostatic charge-discharge profiles at several current densities were determined by using the Equations above. The highest specific capacitance obtained from the CV and GCD is depicted in Figure 46. The maximum areal-specific capacitance from CV is 65 mF/cm² at 20 mV/s scan rate and the GCD is 75 mF/cm² at 0.5 mA/cm² current density.

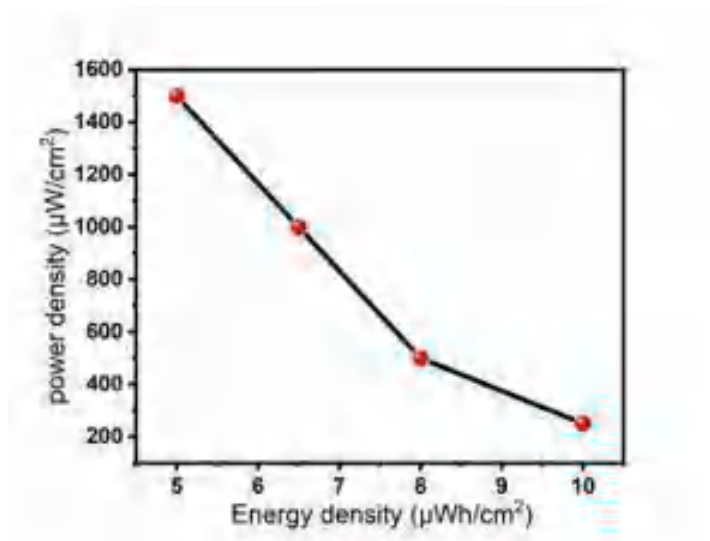


Figure 47: GCD profiles at different current densities

The Ragone plot shown in Figure 47 was produced using the values for the GCD-specific capacitance. The CrN-based symmetric supercapacitor delivered an energy density of about 5 μWh/cm² at the maximum power density of 1500 μWh/cm². The corresponding energy density and power density at different current densities are listed in the table above.

(4) Electrochemical Impedance Spectroscopy Result

The Nyquist plots in Figure 48 depict the CrN thin film supercapacitor both before and following the GCD cycle stability evaluation between a frequency range of 100 Hz to 10⁶ Hz at 0V. The Nyquist plot at a high-frequency section displays semicircles, representing a charge transfer resistance (R_{ct}), and optimum capacitive behavior is suggested at the domain of the low-frequency by the nearly vertical lines. The fitting of the EIS measurements with the equivalent circuit assisted in determining the Equivalent series resistance (ESR), the resistance of the charge transfer R_{ct}, and the Warburg impedance.

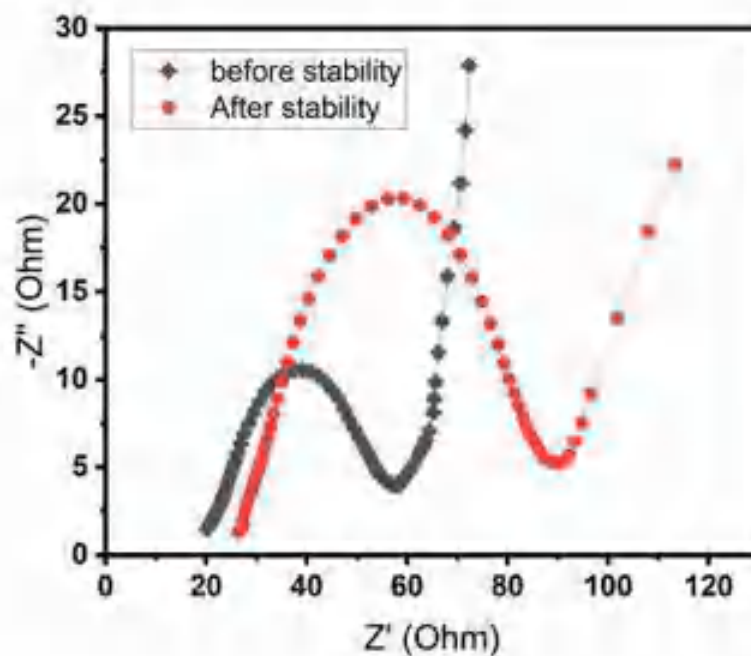


Figure 48: Nyquist plots of the F6-based symmetric supercapacitor before and after 5000 GCD cycles in the frequency range from 1 Hz to 1 MHz

The ESR deduced at a point where the semicircle intersects the X-axis is $20\ \Omega$ before stability in the Nyquist plot representing an effective ionic transport and conductivity. At the low-frequency section, the charge transfer resistance estimated at the depressed semicircle due to the emergence of the kinetic control process is observed to be $40\ \Omega$ indicating commendable electrical conductivity and charge transfer potentials. An R_S and R_{ct} of $24\ \Omega$ and $66\ \Omega$ respectively are observed for the post-stability. These values increase than the obtained result in the pre-stability measurements.

(6) CrN Stability and Efficiency Result

The film displayed an exceptional capacitance retention of $\sim 98.2\%$ after 5000 cycles at a current density of $5\ \text{mA}/\text{cm}^2$ and maintained a Coulombic efficiency of 97.5% , signifying a rapid charge-discharge and an excellent reversibility potential.

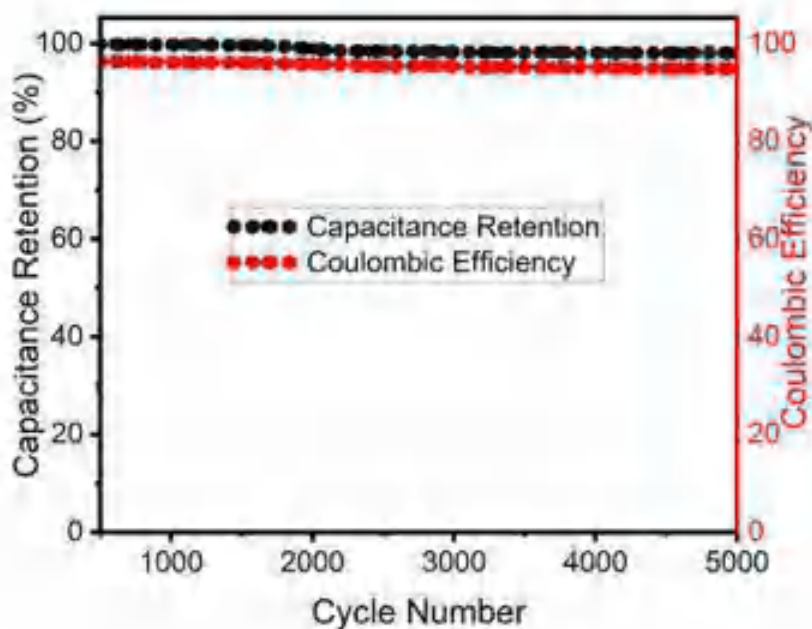


Figure 49: Cyclic stability of the F6-based symmetric supercapacitor of capacitance retention (98.2 %) and Coulombic efficiency (97.5 %) up to 5000 GCD cycles at 5 mA/cm² current density

The film displayed an exceptional capacitance retention of ~98.2% after 5000 cycles at a current density of 5 mA/cm² and maintained a Coulombic efficiency of 97.5%, signifying a rapid charge-discharge and an excellent reversibility potential. In the realm of energy storage research, comprehension of the stability and ion/charge transfer characteristics is critical. Figure 49 highlights the cyclic stability and Coulombic efficiency of the F1-based symmetric supercapacitor, providing a testament to the endurance of the CrN films. After 5000 cycles at a current density of 5 mA/cm², the supercapacitor retains an impressive 98.2% of its initial capacitance, underscoring the robustness of the CrN material in maintaining its storage capability over extended use. Additionally, the Coulombic efficiency remains high at 97.5%, indicating that nearly all the charge stored during the charging phase is released during discharge, which is a desirable characteristic for energy storage devices, emphasizing the efficient charge-discharge reversibility of the supercapacitor. EIS serves as a pivotal technique in this exploration, providing nuanced insights into the interfacial and bulk properties of supercapacitor electrodes. Figure 37 presents Nyquist plots of the CrN thin film-based symmetric supercapacitor, captured both before and after subjecting the device to 5000 GCD cycles. The frequency range extends from 1 Hz to 1 MHz, with the intention of capturing the entire spectrum of charge transfer phenomena within the

supercapacitor. Prior to the stability tests, the high-frequency region of the Nyquist plot reveals a semicircle, indicative of charge transfer resistance (R_{ct}) within the supercapacitor. The diameter of this semicircle is a direct representation of the R_{ct} , and its intersection with the real axis (Z') corresponds to the equivalent series resistance (ESR) of the device. The ESR, estimated to be approximately 20 Ω , points towards effective ionic transport and good conductivity of the CrN films. At lower frequencies, a near-vertical line suggests capacitive behavior dominated by ion diffusion within the porous structure of the electrode [109]. Upon completion of the stability test, the Nyquist plot undergoes noticeable changes. The ESR shows a slight increase, while the R_{ct} exhibits a more pronounced increase from 40 Ω to 66 Ω . These changes could be attributed to modifications in the electrode/electrolyte interface or the electrode material itself due to the prolonged cycling, potentially reflecting a change in the kinetic processes controlling the charge transfer. The EIS and cycling performance data collectively suggest that the CrN thin film electrodes possess both favorable charge transfer properties and remarkable durability, making them suitable candidates for long-term energy storage applications. The slight increase in resistance values post-stability testing suggests a moderate impact on the supercapacitor's internal structure after extensive cycling, which remains an area of ongoing investigation for further optimization of the supercapacitor's lifecycle.

CHAPTER 4

CONCLUSION

The characterization of chromium nitride and chromium oxynitride film structural, optoelectronic, and electrochemical properties grown on Si(001) and fused silica using a radio frequency magnetron sputtering system coupled with highly pure chromium target substrate in argon and nitrogen environment as processing and reactive gases respectively is accomplished. The RF sputtering power was maintained at a constant value and low base pressure throughout the growth while the processing and the reactive gases were controlled during the growth process. The film thickness was obtained from the thickness monitor of the part of the sputtering system and confirmed using a DekTak XT thickness measuring device. The structural characterization of the films by the XRD showed phase orientation of (002) dominance of CrN. A structural phase transition occurs between a cubic CrN to hexagonal Cr₂N crystal structure when the nitrogen flow rate is high while other films showed a phase transition of the Cr₂O₃ compound and SiO₂ compound. The influence of the residual stress and oxidation in the films was observed in the samples which generate a strain stress or compressing bonds between the atoms hence increasing or decreasing the interplanar spacing of the crystallographic planes. Depending on the nitrogen partial pressure present during the growth procedure, the bandgap obtained varied between 0.27 eV and 3.63 eV. These changes in the energy gap of CrN films make them a promising material for use in solar cells because of their broad energy bandgap control. The films also demonstrated switching between n-type and p-type due to the varied growth parameters in both samples.

The CrN-based thin film symmetric supercapacitor electrochemical performance in a 1 M H₂SO₄ electrolyte was extensively assessed using CV, GCD, and EIS techniques. The films showed a remarkable specific capacitance of about 75 mF/cm² at a current density of 0.5 mA/cm² and 65 mF/cm² at a scan rate of 20 mV/sec and praiseworthy EDLC behavior. Moreover, the supercapacitor-based thin films demonstrated impressive power and energy densities along with strong cyclic stability while charging and discharging, highlighting the capacitance efficiency of the fabricated CrN thin film.

In conclusion, this work adds a great deal to our understanding of how to optimize the characteristics of CrN and $\text{CrO}_x\text{N}_{1-x}$ and similar compounds for a wide range of cutting-edge technological uses. Developing more quality and high-performing films by the understanding possibility of customizing growth parameters accordingly, particularly the processing and reactive gases is achieved. This is especially applicable in the fields of renewable energy, photovoltaics, and energy storage. We get closer to realizing the full potential of these extraordinary materials because of our research, which opens the door to more investigation and creativity in this fascinating sector.

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SKILLS

Material Characterization Techniques: X-ray diffraction, Scanning Electron Microscopy, Energy Dispersion Spectroscopy, X-ray Photoelectron Spectroscopy, UV-Vis-IR spectroscopy, Raman Spectroscopy, Vacuum tube furnace, Laser-Induced Breakdown Spectroscopy, Thin film fabrications, Magnetic sputtering system, Electrochemical characterizations.

Software Skills: Python, MS Office Package, Latex, Inkscape, Corel Draw, Mathematica, Origin Package, Advantage, Vesta Package.

Academic Education

•	MSc	Physics	KFUPM	2024
•	BSc	Pure and Applied Physics	LAUTECH	2018
•	SSCE	Certificate	Ilesha Grammar School	2007
•	PSLE	Certificate	Akinyemi Future Hope	1999

Additional Education

Organic Farming	2010
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Honors and Awards

•	Won 2 nd position award and prize in the Graduate student category in the Annual Physics Poster Competition at King Fahd University of Petroleum and Minerals	2024
•	Dean's Academic Award	2018
•	Junior High School Merit Scholarship Award	2004

Research Experience

•	Research and Teaching Assistant	KFUPM	2023
•	Teaching Assistant	Islamic College	2019

- Teaching Assistant I. Ibrahim Int. School 2018

Professional Experience

Position	Company	date
• PO	INEC	2019
• Lab Technologist	ATBU	2019
• Technologist Assistant	Classic system infotech.	2005

MSc Thesis

- Growth and Characterization of Chromium Oxynitride Thin Films Grown by RF Magnetron Sputtering for Energy Harvesting and Energy Storage Applications

Journal Publication

- **W. S. Kamoru**, M. B. Haider, B. Ul Haq, S. H. Aleithan, A.M. Alsharari, S. Ullah, K. Alam* “Structural, Electronic, and Optical Properties of Chromium Oxynitride Thin Films Grown by RF Magnetron Sputtering” Results in Physics, **57**, 107387 (2024).
- Enhanced Supercapacitance Performance of Chromium Nitride Thin Films Electrodes Grown by RF Magnetron Sputtering: Structural, Electronic, and Electrochemical Characterizations (submitted).

Conference Proceeding

- K. Alam*, **W.S. Kamoru**, M.Y. Perdana, S.S. Shah, M.B. Haider “Structural and Electronic Properties of Chromium Nitride Thin Films for High-performance Supercapacitor Electrodes” APS March Meeting, **68**, K45.00002 (2023).
- K. Alam, **W.S. Kamoru**, M.B. Haider, B. Ul Haq “Tuning the Structural and Optical Properties of Chromium Nitride for Advanced Technological Applications”. APS March Virtual Meeting, (2024).

Poster Competition

- **W. S. Kamoru**, O. Alsir, K. Alam* “Structural, Electronic, and Optical Properties of $\text{CrO}_x\text{N}_{x-1}$ Thin Films by RF Magnetron Sputtering”, Annual Physics Poster Competition, Physics department, KFUPM February 14, 2024.

Trade Association & Network

Position	Community	date
• Welfare & Social Director	SCCM	2019
• Treasurer	MCAN	2019
• Member	NIP	2015