

**STUDY OF COBALT DOPED TITANIUM NITRIDE
AND CHROMIUM DOPED TITANIUM NITRIDE
THIN FILMS GROWN BY RF/DC MAGNETRON
SPUTTERING**

BY

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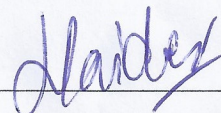


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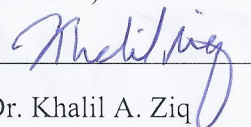


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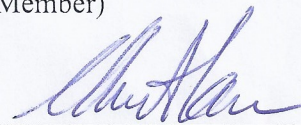
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To my family

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LIST OF ABBREVIATIONS

MBE Molecular Beam Epitaxy

PLD Pulsed Laser Deposition

AFM Atomic Force Microscopy

XRD X-ray Diffraction

XPS X-ray Photoelectron Spectroscopy

GMR Giant Magnetoresistance

B.E Binding Energy

VSM vibrating sample magnetometer

XRR X-ray Reflectometry measurements

ABSTRACT

Full Name : Ebrahim Alhaj Ebrahim Abualgassem
Thesis Title : STUDY OF COBALT DOPED TITANIUM NITRIDE AND
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The work carried out in this thesis involves the thin film growth and study of transition metal doped nitride semiconductors. Main aim of the study was to find the optimum growth condition to form dilute magnetic semiconductor, where the film can be semiconducting and ferromagnetic at the same time. Dilute magnetic semiconductors have potential applications in new branch of devices called Spintronics, where not only charge but spin of the electrons (or holes) can be exploited to fabricate much faster and low power consumption devices. Two sets of materials were studied in this thesis work, cobalt doped titanium nitride and chromium doped titanium nitride. Cobalt doped titanium nitride thin films were prepared by sputtering titanium target using RF powered sputtering gun and cobalt with DC powered sputtering gun in the presence of argon and nitrogen gasses. Chromium doped titanium nitride films were produced the same way except the chromium target was used for DC sputtering, instead of the cobalt target. The doping level in the films was controlled by adjusting the DC power of the sputtering gun whereas RF power for titanium sputtering was the same for all the films. Surface and bulk properties of the grown films were studied using x-ray diffraction, atomic force microscopy, spectrophotometry, x-ray photoelectron spectroscopy, x-ray reflectometry, and vibrating sample magnetometry (VSM). The concentration of cobalt or chromium dopants in the titanium nitride films

effected the optical, chemical, and magnetic properties of the films. A red shift in the bandgap of the cobalt/chromium doped titanium nitride films were observed as a function of cobalt/chromium concentration. X-ray photoelectron spectroscopy confirmed the presence of cobalt in the film and cobalt concentration in the film was estimated to be between (0 to 7) %. Cobalt in cobalt doped titanium nitride films was found to be in a mixed high spin +2 and low spin +3 oxidation state whereas Chromium was found to be in third (Cr^{+3}) and sixth (Cr^{+6}) oxidation state. Magnetic properties reveal a weak magnetization for the films coexisting with the strong diamagnetic background of the substrate. The magnetic response in cobalt doped titanium nitride films was found to be temperature independent for the films with low cobalt concentrations, whereas for the films with higher cobalt concentrations clearly exhibited hysteresis and the saturation magnetization increased at lower temperature. The hysteresis did not exhibit any obvious coercive field, and the films showed the features expected of superparamagnetic or paramagnetic environments at 3-5 K.

ملخص الرسالة

الاسم الكامل : ابراهيم الحاج ابراهيم ابوالقاسم

عنوان الرسالة : دراسة الأغشية الرقيقة من نيتريد التيتانيوم المطعم بالكوبالت و نيتريد التيتانيوم المطعم بالكروم المحضرة بواسطة المغنطرون

التخصص : فيزياء

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تعنى هذه الأطروحة بدراسة وتحضير أغشية رقيقة من أشباه موصلات النيتريد المشوبة بالمعادن الانتقالية. الهدف الرئيس من الدراسة هو إيجاد الظروف المثالية للنمو الأمثل لتكوين أشباه الموصلات المغناطيسية المخففة ، حيث يمكن أن يكون الفيلم شبه موصل وله خواص مغناطيسية في نفس الوقت. أشباه الموصلات المغناطيسية المخففة لديها تطبيقات محتملة في فرع جديد من الأجهزة تسمى حيث يتم استخدام شحنة وعزم الإلكترون وتمتاز هذه الأجهزة بأنها سريعة وأقل استهلاكاً للطاقة. تمت دراسة مجموعتين من المواد في هذا البحث ، نيتريد التيتانيوم المشوب بالكوبالت ونيتريد التيتانيوم المشوب بالكروم. تم تحضير أغشية رقيقة من نيتريد التيتانيوم المشوب بالكوبالت عن طريق قذف هدف التيتانيوم باستخدام مدفع رش يعمل بالترددات الراديوية بينما الكوبالت تم قذفه بمدفع يعمل بالتيار المستمر في وجود غاز الأرجون والنيتروجين. تم إنتاج أغشية نيتريد التيتانيوم المخدر بالكروم بنفس الطريقة فيما عدا استخدام الكروم المستهدف ، بدلاً من الكوبالت المستهدف. تم التحكم في نسبة الشوائب في الفيلم عن طريق ضبط قوة التيار المستمر لمدفع الرش. تمت دراسة الخواص السطحية والكتلة للأغشية المزروعة باستخدام حيود الأشعة السينية ، والفحص المجهرى للقوة الذرية ، والقياس الطيفي ، والتحليل الطيفي الضوئي للأشعة السينية ، وقياس انعكاس الأشعة السينية، والقياس المغناطيسي للعينة الاهتزازية. وقد وجد أن الأفلام تتأكسد بسهولة بعد النمو عند تعرضها للجو. ومن ثم فإن الأغشية المزروعة كانت عبارة عن أكسيد تيتانيوم مخدر بالكوبالت وأكسينيتريد تيتانيوم مخدر بالكروم. أثر تركيز الكوبالت أو الكروم في أغشية نيتريد التيتانيوم على الخصائص البصرية والكيميائية والمغناطيسية للأغشية. لوحظ وجود إزاحة ناحية الطيف الأحمر في فجوة الحزمة لأغشية نيتريد التيتانيوم المخدر بالكوبالت / الكروم كدالة لتركيز الكوبالت / الكروم. أكد التحليل باستخدام مطيافية الأشعة السينية علي وجود الكوبالت في الأفلام وقدر تركيز الكوبالت في الأفلام بين (0-7) في المائة. وقد وجد ان الكوبالت موجود في خليط من حالات الأكسدة المغزلية العالية +2

والدوران المنخفض +3 في أفلام نيتريد التيتانيوم المشبعة بالكوبالت. تكشف الخواص المغناطيسية عن مغنطة ضعيفة للأغشية التي تتعايش مع الخلفية المغناطيسية القوية للركيزة. في تركيزات الكوبالت المنخفضة ، وجد أن الاستجابة المغناطيسية مستقلة عن درجة الحرارة. بالنسبة للأفلام التي تحتوي على تركيزات أكبر من الكوبالت ، لا يُظهر التباطؤ أي مجال قسري واضح ، وتُظهر الأفلام في حالة من المغناطيسية الفائقة أو شبه المغناطيسية عند 3-5 كلفن وتصبح الاستجابة المغناطيسية معتمدة على درجة الحرارة. بينما وجد الكروم في حالة الأكسدة الثالثة والسادسة عند دراسة الأفلام بجهاز مطيافية الأشعة السينية.

CHAPTER 1

INTRODUCTION

1.1 Introduction

1.1.1 Dilute Magnetic Semiconductors

Semiconductor electronic devices such as MOSFETs, FETs, Bipolar junction transistors, etc. are based on the control and manipulation of electronic charge in the semiconductors [1-3]. A new class of devices have been proposed that would be based not only on the charge of the carriers (electrons or holes) in the semiconductors but also on the spin of these charge carriers, this new class is called Spintronics. Manipulation of spin is relatively faster and would not cost a lot of energy, so spintronics based devices are thought to be much faster in speed compared to their traditional counter parts and would cost less energy to operate. To fabricate these devices, charge carriers should be spin-polarized with large enough coherence length such that carriers maintain their spin polarization in the material. Reducing the size of the transistor became useless in improving the work of the old transistors, this made scientists turn to another way to improve the electronic devices by utilizing the spin of the electron. Datta and Das proposed in 1980's the idea of Spin Field Effect Transistor based on the spin of electrons, which is an improved version of the common transistor [4].

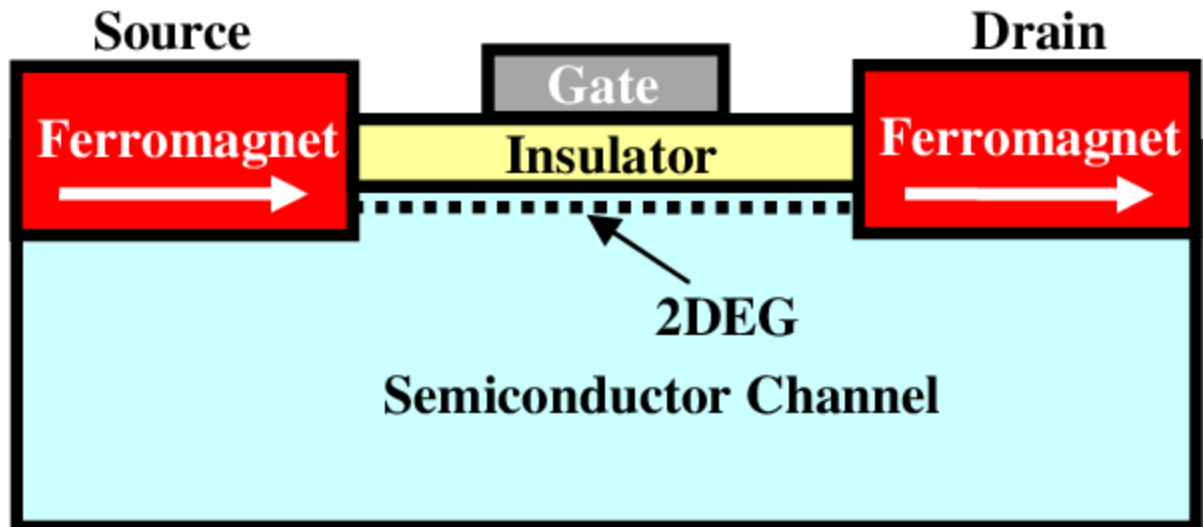


Figure 1 Basic form of a spin field-effect transistor [5].

Figure 1 shows a schematic diagram of FET. There is ferromagnets are used as source and drain, and the current can pass between these two through a semiconductor channel manipulated via gate voltage. The carriers inserted into this channel are spin-polarized and accepted readily by the drain, resulting in an ('on' state). As a minimal gate voltage is applied, however, the spins begin to rotate or precess due to their interaction with the lattice of the semiconductor. By the time their spin is no further aligned in the original configuration when they approach the gate, and the drain no longer accepts them (the 'off' state). As opposed to a MOSFET, this device's utility derives from the fact that it takes relatively little energy to process spins. The important key elements of spintronics are the Injecting, manipulating, transferring, and detecting spin-polarized carriers through a semiconductor device[5]. The ferromagnetic source substance is required to make these spin-polarized carriers but ferromagnetic metals are inadequate sources because of a lack of congruence in conductivity between a semiconductor and a metal[6]. This issue can be resolved by using a magnetic semiconductor source. Magnetic semiconductors for example Chromium chalcogenides (CdCr_2Se_4 , CdCr_2S_4) and Europium (EuO , EuS) have been

researched for their interrelation among semiconductor and magnetic properties. Nevertheless, these substances are not salutary technologically and the growth processes are difficult[7, 8].

A new class of materials that appeared in the early 1980s known as dilute magnetic semiconductors (DMS) which consists of II-VI alloys doped by manganese and has the form $A_{1-x}Mn_xB$ for example $Hg_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xTe$. There are a number of reasons that made these compounds attractive such as their band and lattice parameters can be tuned readily by adjusting the composition of the alloy, allowing them to be suitable for the heterostructure devices[9]. Furthermore, the Mn-related electroluminescence is very effective, making them appealing for optoelectronic applications. The ferromagnetism observed in these substances is driven by hole-mediated exchange and reported in $Zn_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xTe$. But on the other hand, II-VI as DMSs have low Curie temperatures $T_C \sim 2$ K, and the difficulty of doping both p-type and n-type restrict their use in practical applications[9-11]. This set the stage for further investigation into III-V substances as potential DMS candidates. In the early 1990s, the field experienced its first boom, coinciding with the second generation of DMS substances. The use of low-temperature molecular beam epitaxy (LT-MBE) technique has overcome the problem of insolubility of transition metal impurities in III-V semiconductors, Ohno et al.[12] reported ferromagnetism in p-type Mn-doped InAs up to $T_C = 7.5$ K. After the success growth of $In_{1-x}Mn_xAs$ using LT-MBE this led to development of Mn-doped GaAs with higher T_C [13]. The material (Ga, Mn) As DMS is one of the ferromagnetic semiconductors most fully known and potential for use in spintronic. The biggest challenge is that it is confirmed that the maximum (Ga, Mn) As Curie temperature is 173 K, was reported owing to development

in MBE growth and the post-growth annealing techniques by Jungwirth et al. (2005b)[14], and Wang et al. (2005a)[15] well below room temperature. Nonetheless, spin-related devices based on (Ga, Mn) As, like spin-valve, spin-FET, and spin-polarized light emitter (spin-LED), were seen at low temperatures.

Around the year 2000, the field encountered a big boom based on the Zener model of ferromagnetism by Dietl et al[16]. While materials like Mn-doped InAs and GaAs were extensively researched throughout the 1990s and into the present, there is another generation of DMS materials appeared throughout the last twenty years. This new set of DMS materials primarily consisted of the wide-gap nitrides (such as GaN) and oxides (such as ZnO and TiO₂) doped by 3d transition metals, primarily Fe, Co, and Mn. Following Matsumoto et al.[17] reported a high-temperature ferromagnetism in Co-TiO₂, and Dietl's prediction that p-type, ZnO and GaN doped by Mn could achieve a T_C above room temperature, a number of DMS materials with wide-gap have been reported with ferromagnetism at and above room temperature[18-21]. The material Co-ZnO, Mn-ZnO, Mn-GaN, and Fe-GaN received special consideration. This could be linked to a combination of causes, the early predictions of room temperature ferromagnetism in these materials by Dietl and Sato even if there is no additional carrier doping. Furthermore, GaN and ZnO based DMS materials are compliant with current semiconductor heterostructure technology.

Zener suggested a model for ferromagnetism in dilute alloys of a transition metal that was based on the exchange interaction between localized spins and the carriers. The model consists of three significant ideas: First the lowest energy state in an isolated atom is provided by the electronic state in which an incomplete d-shell had the highest spin,

which implies that all spins are aligned. The second one is the exchange integral between neighboring atoms' d-shells often results in antiferromagnetic order. The last one is an imperfect shell's spin is closely bound to the conduction electrons. The ferromagnetism is achieved when this pairing dominates over the direct exchange. However, this model was later discarded, since this model ignores the itinerant existence of the magnetic electrons and the quantum oscillations of the electron spin polarization around localized spins, all of these are now accepted as fundamental components of the theory of magnetic metals[22, 23].

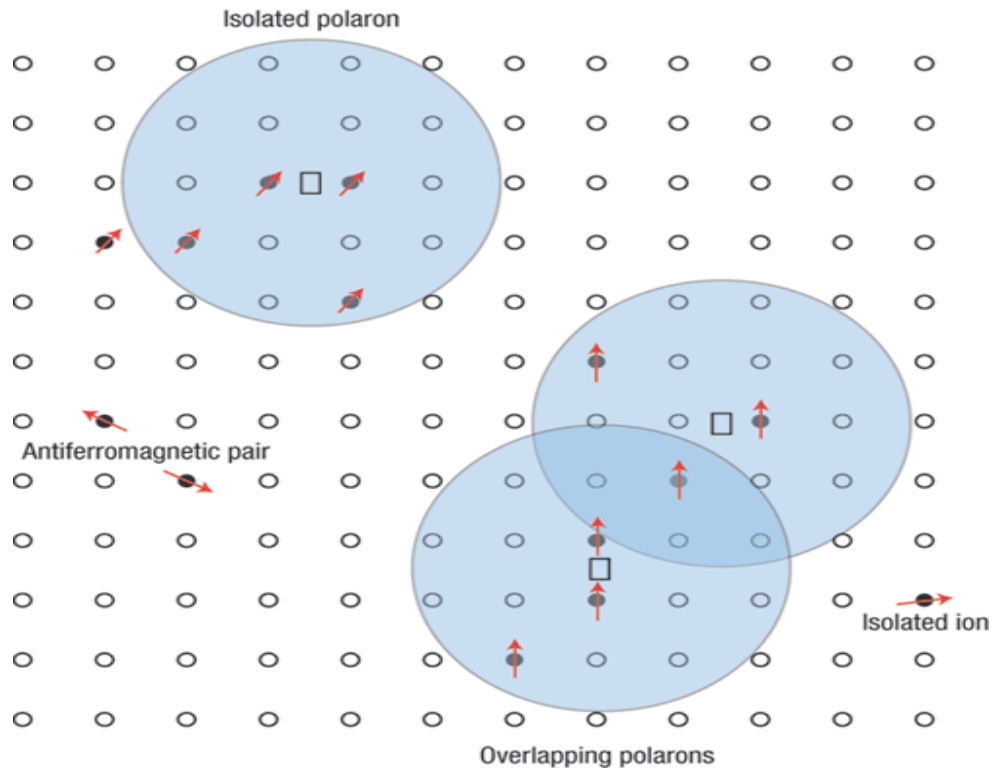


Figure 2 Magnetic polaron representation. The small circles represent Cation sites, and the squares represent unoccupied oxygen sites[24].

Coey proposed a model based on the exchange interaction between atomic spin moment and strongly coupled narrow impurity bands. The schematic interaction in oxides is shown in Figure 2, where defects like (oxygen vacancies) serve as electron sources. These

electrons are in hydrogenic orbitals, and their particular orbits broaden out into small impurity bands as their concentration grows. There is an exchange interaction between the electron and magnetic ions when they are lying in the electron orbit. If the number of magnetic spins is a significant enough the electron is fully spin polarized. In addition, the atomic magnetic moments have an indirect exchange interaction, which is mediated by the carriers, resulting in their ferromagnetic ordering[24].

Another approach is to dope semiconductor materials with rare earth elements or transition metals to form magnetic semiconductor. A material in which carriers can be manipulated like in a traditional semiconductor but at the same time, the carriers are spin polarized.

DMS is a material that has a semiconducting and magnetic characteristic jointly in conjunction. DMSs are formed by lightly doping a semiconductor with the transition metal elements and owing to their possible use in spintronic applications and may radically change the design of conventional semiconductor devices, this field have become the focus of intensive study over the last few decades [9, 25-27]. Dietl et al. [16] have modified a model of p-d Zener exchange for understanding ferromagnetism in p-type DMS materials. The localized spins of Mn and the delocalized free carriers are considered as interacting spin subsystems in this model, and the exchange energy $N_0\beta$ is used to parameterize the interaction, so-called p-d exchange expression. Where N_0 is the total density of the cation site number and the p-d exchange integral is β . The magnetic moment created by Mn spins aligning in parallel reduces the carrier energy, splits the valence band and raise the Mn spin subsystem energy. As the temperature is decreased, the energy difference between the Mn spins and the carriers reduces, and both energies at T_c are become equal. T_c is expressed as follows when these energies are equated at a mean-field level:

$$T_C = xN_0S(S + 1)A_F\rho_s\beta^2/12k_b - T_{AF}$$

Where , A_F is the Fermi liquid parameter, S represent the total spin of the magnetic dopant, k_b is the Boltzmann constant, T_{AF} is the antiferromagnetic ordering temperature, $\rho_s(E_f)$ is the density of states for the free carrier at Fermi level. Large E_f and the p–d exchange integral with high value are the keys to get high T_c at this degree of approximation. Higher T_c can be achieved easier in p-type than n-type semiconductors because $N_0\beta$ is usually larger than $N_0\alpha$. Dietl's theory can be generalized to a range of p-type DMS and is used to estimate T_c for a number of candidates. It was effective in materials (Ga, Mn) As, and (Zn, Mn)Te. Zener model suggests that semiconductors with the large bandgap doped by manganese display critical temperatures over 300 K when there is enough high hole density can be reached $10^{20}cm^{-3}$ [16, 28]. This model suggests the lattice constituents will be randomly replaced by the doping atoms. Ferromagnetism in the semiconductors of manganese compounds allows to understand the spin-related phenomena and the magnetic in DMS with an accuracy unique to III-V compounds and responds to questions relevant to the origins of magnetic interactions that proceed to a T_c of up to 110 K for just 5 percent of a manganese concentration [16].



Figure 3 Curie temperature computed values for separate p-type semiconductors having $3.5 \times [10]^{20}$ holes per cm^3 and 3.5 percent of Mn [16].

Figure 3 illustrates the Curie temperatures predicted by Mean Field Theory for different DMS candidates. T_c was calculated based on Mn doping with a high p-type doping. III-V Nitrides like GaN, as well as oxides like ZnO, are among the candidates with the highest T_c . A lot of DMS studies have been focused on nitrides and oxides as a result of these forecasts. In this review, we looked at TiN, as possible candidate. There is a lot of research done on DMSs materials, but the research interest can be reduced to two primary groups of materials among the many kinds of DMS materials presently being investigated: (1) narrow-gap III-V semiconductors, mostly InAs and GaAs, doping by Mn. Mn impurities act as both electrical and magnetic dopants. Due to a number of motivating functionalities derived from the carrier-mediated ferromagnetism and pretend in diverse proof of concept devices and a powerful technological background this category of materials has become the most hopeful candidate for DMS materials technology application. Despite significant

developments over the past 15 years, however, their T_C stay below room temperature [29], (90 K in InAs [30] and 185 K in GaAs [31]). (2) wide-gap oxides (especially ZnO) and nitrides (especially GaN) doped with 3d transition metals. The scenario is much more uncertain for the wide-gap oxides and nitrides, while the vast majority of the reports claim that ferromagnetic order exists above room temperature or even at room temperature, there is no unanimity regarding the ancestry of such ferromagnetism [27, 29, 32]. Nevertheless, after several inquiries, the cause and regulation of ferromagnetism in DMSs is still the most contentious research subject these years. Latest theoretical studies indicated that ferromagnetism well above room temperature can be exhibited in nitride and oxide diluted magnetic semiconductors, and some of the recent report include Cr-AlN, Cr-GaN, Mn-GaN, that has been conducted and is in agreement with theoretical research [24, 26, 27, 33, 34]. There were few attempts of doping titanium nitride semiconductors with transition metals as the DMSs to analyze their magnetic demeanor. In this article, we looked at one such future candidate, TiN. We reviewed some models for explaining magnetism in DMS substances, which proceeds to a consideration of promising DMS materials. Two sets of materials were studied in this thesis work, cobalt doped titanium nitride and chromium doped titanium nitride. Then the experimental results obtained from this work are discussed.

1.1.2 Titanium nitride

Titanium nitride is a versatile material with a wide band gap, also has a beneficial mingling of physicochemical characteristics such as high strength, strong wear resistance, very high visible transmission, good chemical inertia and corrosion resistance and low resistivity. Due to its physical characteristics, TiN is a desirable material for use in diverse

photoelectric devices, also is used in thin film resistors, decorative coatings, optical filters and protective coatings [35-38]. Additionally, TiN has been used as electrical interconnects and surface layers in cardiac valves, orthopedic prostheses, and some other biomedical devices, because of the fundamental biocompatibility and hemocompatibility [39, 40]. TiN films displayed remarkable optical properties as the luster and color of TiN films differ with the ratio of N/Ti atoms such as, the luster and color of TiN films display gold color when the ratio of N/Ti atoms is equal one. So, it has a variety of uses in the area of architectural design and is utilized as a decorative film, like ceramic tile or glass sculpture, sanitary cloth and stainless-steel mirror.

The characteristics of TiN differ depending on the quantity of nitrogen incorporated as an outcome of the faulty filling of the sites available as well as dependent on the growth conditions.



Figure 4 Crystal structure of titanium nitride[41].

TiN can exist in several phases but the primary phase of the TiN crystallizes in the rock-salt structure and in the stoichiometric material titanium nitride has a lattice parameter (a) of 4.24 Å shown in Figure 4. The Ti atoms form a face-centered-cubic (FCC) lattice in this lattice, while the N atoms form an equivalent lattice that is displaced in the direction of (100). This implies that each Ti atom has six N atoms surrounding it, one for each coordinate direction. Since Ti and Nitrogen appear in this lattice configuration in a 1:1 ratio, chemically pure (or stoichiometric) TiN can contain 50 percent Ti and 50 percent N[42]. Titanium is a transition metal and has three valence electrons. The core electrons in the 4s and 3d states, are not bound strongly to the Ti atom and therefore can be accelerated

by such an electric field. Due to that and structure of the TiN make this material become conductive. The electrical resistivities for single-phase titanium nitride films have been reported to be at the range of 18 to $10^4 \mu\Omega\cdot\text{cm}$ [43]. The optical bandgap of the TiN is found to be varying between 2.7-4.06eV depending on the growth conditions.

The properties of the material can have a change when the impurities are added to it. Doping a material such as TiN by transition metal can led to different properties do not present in un doped TiN. Some research confirmed that the film's electrical and optical properties are highly correlated with the film's crystalline quality surface morphology, internal stress and preferred orientation. The production of excellent quality films is therefore the basic principle for supporting its broad use [37, 38, 44].

CHAPTER 2

EXPERIMENTAL AND LITERATURE REVIEW

Dilute magnetic semiconductors have attracted a lot of interest in research due to their potential use in spintronics application, several techniques like (Molecular beam epitaxy, pulsed laser deposition, chemical vapor deposition (CVD), ion beam assisted deposition, physical vapor deposition (PVD), and DC/RF magnetron sputtering) have been used to synthesize these materials and study their properties.

Ohno et al. [12] have investigated the magnetotransport properties of the manganese doped Indium arsenide films prepared by MBE. They concluded that, the abnormal Hall effect, which occupies the Hall resistivity from low temperature (0.4 K) to virtually room temperature, and the creation of partial ferromagnetic order about 7.5 K are all manifestations of the interaction between the Mn 3d spins and the holes. Their success in fabricating a truly dilute magnetic semiconductors started a flurry of research in Mn doped GaAs thin films. A lot of research was performed in GaMnAs to increase the Curie temperature (T_C) of this material with some success but still the Curie temperature of GaMnAs is far below room temperature (~ 175 K). In 2000, by using Zener's model Dietl et al. predicted that wide bandgap materials like ZnO and GaN when doped with transition metal elements like Mn could lead to ferromagnetic semiconductor with T_C well above room temperature[16].

Matsumoto et al. [17] have prepared thin films of titanium dioxide doping by different concentrations of cobalt in single crystals of $\text{SrTiO}_3(001)$ and $\text{LaAlO}_3(001)$ as substrates using the MBE technique and studied the properties of the films as a function of doping level. They found that the grown films are conductive and has a positive magnetoresistance at 2 kelvin about 60%. The resistivity is found to be between 0.1 to 1 ohm-cm, where the carrier concentration is about $10^{18}/\text{cm}^3$. The films remain ferromagnetic above room temperature.

Sasaki et al. [45] have used MBE to grow GaN films doped by Mn on the sapphire (0001) substrates, with ammonia as the nitrogen supply. They reported critical temperatures around 1000 K. The temperature dependencies of magnetization illustrate coexistence of paramagnetic and ferromagnetic phases. Nevertheless, it is still unknown if the high-temperature ferromagnetic process is due to the presence of ferromagnetic metal accumulates trapped in the host GaN lattice or to a (Ga,Mn)N ternary alloy.

Liu et al. [34] have grown Cr-AlN and Cr-GaN thin films on sapphire (0001) and 6H-SiC (0001) substrates at different concentration of Cr to study their properties at different temperature. They found that both Cr-AlN and Cr-GaN thin films exhibits ferromagnetism at over 900 K and they attributed the magnetic behavior to the substitutionary defects of Cr.

Haider et al. [33] have grown GaN films doping by Cr on sapphire (0001) substrate at different temperatures with varying the flux ratio of Ga/N to study the effect of the growth conditions for the grown Cr-GaN films. They found that extremely conditions Ga-

rich or N-rich result in weak magnetic properties. While other, marginally metal-rich or N-rich conditions offer at least up to 300 K ferromagnetic behavior. The morphology of the surface is highly dependent upon the concentration of surface Ga. They attributed the observed behavior of FM in the films to FM exchange between magnetic ions of chromium in GaN semiconductor.

Ganesh et al. [46] have grown nanocrystals of pure and gallium nitride doped by cobalt. They found that in the pure and less (5 mol%) doped GaN nanocrystals there is no impurity phases but there is a secondary phase when doped by 8 mol%. The crystal size is found varies from 1 to 140 nm in all prepared nanocrystals. The band edge emission is decreased when the dopant concentration is increased, they attributed the decrease in the band gap to the defect states or presence of traps in the band gap. Magnetic Co doped GaN measurements have demonstrated ferromagnetic behavior up to room temperature and they attributed the ferromagnetic behaviour to exchange interaction between electrons or holes from the valence band and localized d-spins of cobalt ions.

Ghobadi et al. [47] fabricated TiN thin films using DC reactive magnetron sputtering and analyze the influence of substrate temperature on the semiconductor and optical properties as well as the 3-D surface morphology. by using AFM, the images showed that at different deposition temperature the film's surface topography was changed. And by increases substrate temperature to 400°C from room temperature, the optical band gap energy reduced to 3.43 eV from 04.06 eV on account of the surface effects and the increase of the grain size.

Kavitha et al. [48] They prepared TiN thin films using reactive DC magnetron sputtering to study their properties. They found that the electrical, microstructural,

chemical, optical properties of the films that prepared are heavily dependent on partial nitrogen pressure. XPS analysis observed existence of different phases in the thin films, sub stoichiometric and stoichiometric TiN thin film, at low partial nitrogen pressure (0.3 Pa) and at increasing partial nitrogen pressure (0.6 Pa) respectively. The optical bandgap in stoichiometric films decreased from 2.9 eV into 2.7 eV. With rising nitrogen content, the resistivity gradually reduced, approaching 1800 $\mu\Omega$ a minimum for thin TiN stoichiometric film.

Ponon et al.[49] have deposited a TiN_x utilize a titanium target in an environment of nitrogen by reactive sputtering. As the nitrogen content increases, conductivity is found to improve. Then films were annealed, which varied the anneal's time and temperature. Resistivity is found to decline during post-deposition annealing with higher temperature and longer annealing time. The deposit of TiN_x at high nitrogen flow rate was reported to be morphologically, thermally and electrically more stable when the flow rate of nitrogen was high compare with those deposited at lower nitrogen flow levels.

Solovan et al. [50] have used reactive magnetron sputtering to form TiN thin films. They showed that from indium can made an Ohmic contact to TiN thin film. Also they showed that TiN thin films exhibited n-type charge carriers with concentration of $2.88 \times 10^{22} \text{cm}^{-3}$ and the resistivity at room temperature is $\rho = 0.4 \Omega$ at temperatures between $295 \text{ K} < T < 420 \text{ K}$ they found the activation energy is 0.15 eV. They found that the TiN thin film material has a direct band gap semiconductor, and the band gap is about $E_g = 3.4 \text{ eV}$.

Jeyachandran et al. [51] have used DC magnetron sputtering to deposit TiN thin films under different N_2 concentration conditions (0.5–34%). Golden colored stoichiometric TiN films were acquired at small N_2 concentration of 0.5 percent, but when the concentration of N_2 increased the non-stoichiometric TiN_x phases were founded. nevertheless, regardless of the concentration of N_2 , when the thickness of the film increased the TiN stoichiometry in the films increased. Lower thickness films are noticed to be amorphous and when thickness of the films is increased the crystallinity was found. The deposited TiN films with a small concentration (0.5 percent) of the N_2 displayed Soft and regular morphology with tightly packed crystallites. By raising the concentration of N_2 were observed a different characteristic for example bubble precipitates, after bubble burst morphologies and needle type crystallization. Nonetheless, uniformity evolved at high N_2 concentration conditions in the increased thickness of the films.

Zhao et al. [36] have deposited TiN coatings on the glass substrates using ammonia (NH_3) and titanium tetrachloride ($TiCl_4$) as precursors using atmospheric pressure chemical vapor deposition to investigate the prospect of low-E TiN coatings. They found that the electrical resistivity decreased, and the concentration of crystals increased, when the flow of $TiCl_4$ and substrate temperature was increasing. The optical transmission of the films depended heavily on the substrate temperature and the flow rate of the gas, the electrical conductivity is found to be around $34.5 \Omega/m$ in the optimum conditions, where the optical transmittance in the visible range is about 50% and the infrared reflectance in above the 3000 nm is higher than 50%.

Lal et al. [52] have used ion beam assisted deposition to prepare TiN thin films in the range of temperature $77 \leq T \leq 300$ K. Their results showed that the films' residual

resistivity ρ_0 decreases with increased nitrogen partial pressure. The films demonstrate the quadratic temperature behavior of the resistivity inside the tested range of temperatures.

Gu et al. [44] have used direct-current reaction magnetron sputtering technique to prepare TiN thin films on a glass substrate as well as a Si substrate with varying Ar/N₂ gas flow rate. They found that, XRD indicated that, when the Ar/N₂ ratio decreasing, the diffraction strength of [111] plane slowly decreased, whereas [200] plane rose, and the grown films on Si substrates showed preferable crystalline goodness than films grown on the glass substrates. Advancement of the Ar/N₂ ratio helps to improve the rate of deposition and the apparent roughness of the surface was observed once the ratio was up to 49. Photoluminescence spectra indicated greater intrinsic emission and smaller emission of defects in TiN films on silicon substrate. In addition, when the Ar/N₂ flow rate ratio rose the resistivity of TiN films was clearly decreasing, particularly films on Si substrate.

Shapovalov et al. [53] have studied the effect of nitrogen consumption as well as current density on the structure of TiN films grown by reactive magnetron sputtering at constant current with a hot target. They found that TiN phase of a cubic crystal system is found to form in the films. Increasing current density contributes to the crystals being textured parallel to the [1 1 1] plane in the films, and there is a significant increase in the stiffness and modulus of normal elasticity.

Farhadizadeh et al. [54] have doped titanium nitride by transition metal elements (TM = V, Cr, Mn, Zr, Nb, Mo, Hf, Ta, W, Re and Os) to describe the structural, mechanical and electronic properties and phase stability. They found that the highest hardness still lower than pure TiN, bond population plays an essential role in hardness, it is seen that the value of the population is not the only factor to estimate or compare the hardness. Finally,

it was shown that the doped atom has no substantial effect on nitrogen charge whereas titanium charge is quite dependent on the doped atom.

Li et al. [55] have prepared Mn doped TiN thin films using plasma assisted molecular beam epitaxy. They have found that post growth annealing in nitrogen plasma reduces the nitrogen vacancies, enhances Mn incorporation on Ti lattice site and hence increases the magnetization of the sample.

Wu et al. [56] have studied manganese doped TiN thin films grown on MgO(001) by plasma-assisted molecular beam epitaxy. They reported Curie temperature of their films to be much larger than 380K and the ferromagnetism was not due to magnetic clusters in the films instead it was the intrinsic ferromagnetism originating due to Rudermann-Kittel-Kasuya-Yosida (RKKY) type long range coupling of Mn moments with the conduction electrons. They have not discussed any contribution of defects in the conduction electrons

Yan et al.[57] prepared nanocrystals iron doped TiN chemically by calcinating nanotubular titanic acid precursor in flowing ammonia. They found that the nanocrystals Fe-doped TiN demonstrate ferromagnetic properties at room temperature. They attribute the ferromagnetic to structural defects and it might be possible to change the magnetic and electromagnetic characteristics by modifying the production of structural defects.

Maarouf et al. [58] have prepared thin films of titanium nitride doping by different concentrations of iron. They found that the undoped and low doped films showed a positive magnetoresistance and at a high concentration of iron the film showed negative magnetoresistance, this was attributed to the formation of magnetic polarons that were aligned ferromagnetically.

2.1 Objectives

The main objective of this work is to grow cobalt doped titanium nitride and chromium doped titanium nitride thin films by RF/DC magnetron sputtering and study their properties. We will study the influence of cobalt (or chromium) doping on the, optical, structural, and magnetic properties of Co-TiN (Cr-TiN) films.

Below are the main objectives of our proposed work:

- 1) Growth of cobalt doped titanium nitride and chromium doped titanium nitride thin films by RF/DC magnetron sputtering with varying cobalt and chromium concentration.
- 2) Study the optical properties of the grown films as a function of cobalt (or chromium) doping.
- 3) Study the effect of cobalt (or chromium) doping on the surface morphology of the films.
- 4) Investigate the crystallinity of the grown films by XRD.
- 5) Investigate the chemical composition of the grown films by XPS.
- 6) Measurements of the magnetization of the grown films and study the effect of cobalt (or chromium) concentration on the magnetic properties of the films.

2.2 Experimental Techniques

2.2.1 Sputtering system

There are several techniques to deposit thin films of inorganic elemental or compound materials, for example physical vapor deposition, chemical vapor deposition, molecular beam epitaxy, e-beam evaporation, thermal evaporation and sputtering of target onto a substrate. Magnetron sputtering is used to deposit films onto a substrate by sputtering elemental or component target materials. The film obtained are mostly uniform with a high degree of homogeneity with high adhesion, high purity, high rate of the deposition, and ease of controlling sputtering conditions.

The secession of atoms from the surface of particular solid material nicknamed the target or source, by means of its bombardment by the energetic ions at low pressure is defined as the sputtering phenomenon, these ejected atoms form a film after losing their momentum when they arrive at the substrate.



Figure 5 Schematic diagram of magnetron sputtering chamber.

2.2.1.1 General aspects and principle of the magnetron sputtering process:

In the sputtering operation the gas ions are pushed through plasma into a target composed of the substance to be deposited. The material is mounted on a substrate in the vicinity after sputtered (removed) from the target. The method is carried out in a closed tube, which is pumped downward to a base vacuum pressure prior the beginning of the deposition (Figure 5). In order to allow plasma ignition, argon gas is sent in into the chamber reach to a pressure of 0.5 Pa ... 12 Pa. Some of those ionized $\text{Ar}^{\pm}$ ions are possible via natural cosmic radiation. A negative potential of up to a few hundred volts is given to the target in the DC-sputtering, consequence the Ar^{-} ions are directed toward the target surface and create target atoms that condense to form thin films on the substrate; furthermore, they produced secondary electrons, leads to allow the gas to ionize further. The DC-sputtering shall be

limited to conducting materials only such as doped semiconductors or metals. Magnetron sputtering deposition techniques are commonly used in manufacturing processes as well as in the production or treatment of advanced material [59].

2.2.2 X-ray diffraction

In 1912, Max von Laue and Co. noticed that crystalline substances behave as three-dimensional diffraction wattle for X-ray wavelengths close to plane spacing in a crystal lattice (Friedrich et al. 1912).

X-ray diffraction is now a popular technique for studying the structures of crystals and atomic spacing. X-ray diffraction is a high-tech, non-destructive testing method that analyzes a broad variety of materials like metals, fluids, minerals, pharmaceuticals, solar cells, plastics, polymers, catalysts, ceramics, semiconductors, and thin-film coatings. The method finds countless practical applications in a number of industries like aerospace, microelectronics, power generation, etc. XRD analyzes can readily identify the presence of defects in a particular crystal, its level of stress resistance, its size and degree of crystallinity, its texture, and virtually every other component relevant to the fundamental structure of the sample [60].

X-ray diffraction is based on monochromatic X-ray interference constructively and a crystalline sample. Shown in Fig 6 is the diffractometer device schematic diagram. The X-rays are emitted by a cathode ray poop, filtered to provide monochromatic radiation, concentrated and guided towards the sample.

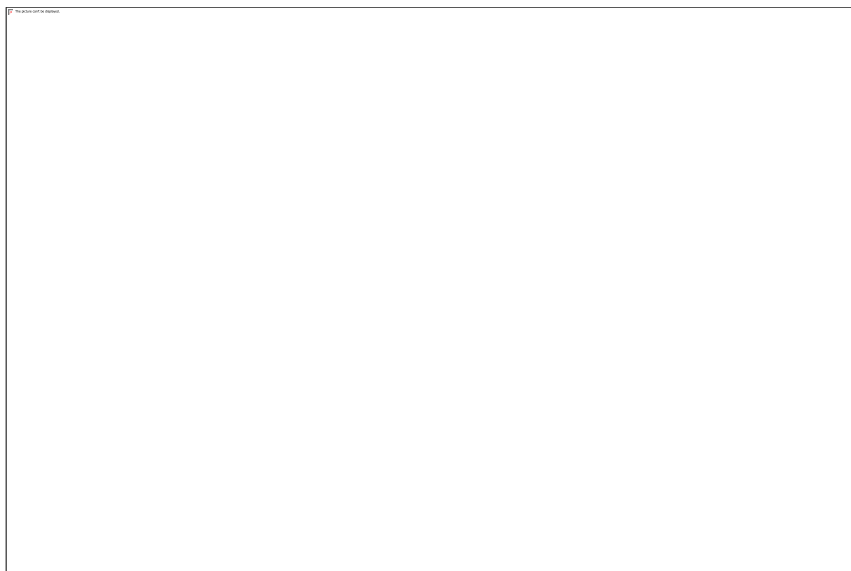


Figure 6 Schematic diagram of a diffractometer[60].

The incident rays contact with the atoms in the sample creates constructive interference with a diffracted ray when conditions follow Bragg's law:

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

where θ , n , λ , and d are the diffraction angles, an order of maxima, the wavelength of the X-rays, and lattice spacing, respectively. This law refers to the wavelength of electromagnetic radiation at the angle of diffraction and the spacing of the lattice in a crystalline object. The X-rays that diffracted then are identified, stored, and counted by scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice have to be achieved. Converting the diffraction peaks into d -spacings enables the compound to be defined, as each compound has a set of specific d -spacings. This is usually accomplished by comparing the d -spacings with regular reference patterns. There are three main elements of X-ray diffractometers: An X-ray detector, an X-ray tube, and a sample holder [60].

2.2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS or ESCA) has been a well-known and commonly performed surface analytical technique that offers a quantitative elementary study of the solid sample's outermost atomic layers and the likelihood of identifying the chemical state of the surface elements. XPS owed its categorization to Einstein's 1905 clarification of the photoelectric effect, and the technique actually has quite a long history which can be linked to contemporary measurements wherein the photoelectrons were excited from the solid by either gamma rays or X-rays. The photoelectric effect has grown into one of our most effective methods for identifying the electronic structure and composition of matter since the late 1950s, with Kai Siegbahn winning the Nobel Prize for XPS production in 1981 [61, 62].

2.2.3.1 Principles of XPS

The technique of XPS is based on the method of photoemission. A high energetic X-ray beam is incident on the material and electron of the core levels of the atoms of the sample absorb the X-ray photon energy $h\nu$ and ejected with kinetic energy and by using electron spectrometer the photoelectron can be analyzed[63, 64].

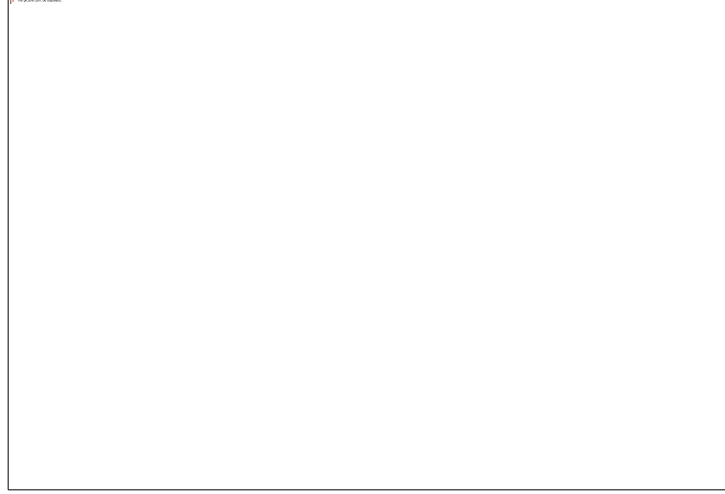


Figure 7 Schematic description of XPS phenomenon of solid surfaces of the related energy concepts[64].

Shown in figure 7 is a vacancy created by an X-ray with energy, $h\nu$, at the core electron level that has binding energy E_b . The ejected core electron will have kinetic energy E in the vacuum and can be written in term of the sample's working function, ϕ_S by $h\nu - E_B - \phi_S$. According to Figure7 the analyzer with work function ϕ_A can measure the kinetic energy E_{kin} by this relation[63, 64]:

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

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

Where ϕ_A is the Analyzer's work function, $h\nu$ represents the x-ray energy from the source, due to their comparatively high energy and narrow width, $Mg K_\alpha$ and $Al K_\beta$ are the two commonly used sources. E_{kin} and E_B are the kinetic energy of the released electron and binding energy, respectively. Using an analyzer to measure E_{kin} and via this equation, the E_B can be calculated because the work function for a particular XPS setup is constant and acts as a reference point. Studying the kinetic energy of an ejected core electron provide a

huge knowledge about the material[64]. Table.1 shows a common radiation sources with their properties.

Table 1 Common properties of radiation sources of $Mg K_{\alpha}$ and $Al K_{\beta}$ X-ray [64].

x-ray source	$Mg K_{\alpha}$	$Al K_{\beta}$
Energy (eV)	1253.6	1486.6
Width (eV)	0.70	0.80

2.2.3.2 Depth profiling

A depth profile can be achieved in an expression of XPS technique of the sample by using an ion beam gun with XPS measurements. The substance is engraved, using the ion gun, for a period of time, the ion gun would then be turned off to obtain XPS spectra. Each ion gun cycle exposes a new surface, such that the structure of these surfaces can be defined by examining the XPS spectra that obtained.

2.2.3.3 Chemical Shift

A particular peak's binding energy relies not just on the element but also on the atoms' energy state and chemical environment. In the XPS spectrum, any alteration in the state and chemical atmosphere that disturbs the energy level of the atom will induce a subsequent difference. This binding energy variance is referred to as a chemical shift [63].

2.2.4 Atomic force microscopy

Atomic force microscopy (AFM) is an innovative method for the surface characterization for the material at the atomic scale. AFM was introduced by Binnig et al. in 1986 and

played a significant role in areas of science such as molecular biology, solid-state physics, and material science. It produces images for Non-conductive materials and no need for staining or chemical etching compare with other surfaces technique. AFM is a tool for inspection of surface topography but can also make a major contribution to understanding the properties of surfaces and interfaces. The instrument is based on the idea that interatomic potentials are formed between the tip atoms and the surface atoms when a tip, inserted at the end of a spring cantilever, is positioned inside the interatomic secession between the sample and the tip. The interatomic potential causes the cantilever to swing down and up with the variations in the surface's contours as when the tip travels over the surface. Thus, the topographic characteristics of the surface can be traced out by calculating the deviation of the cantilever [65, 66].

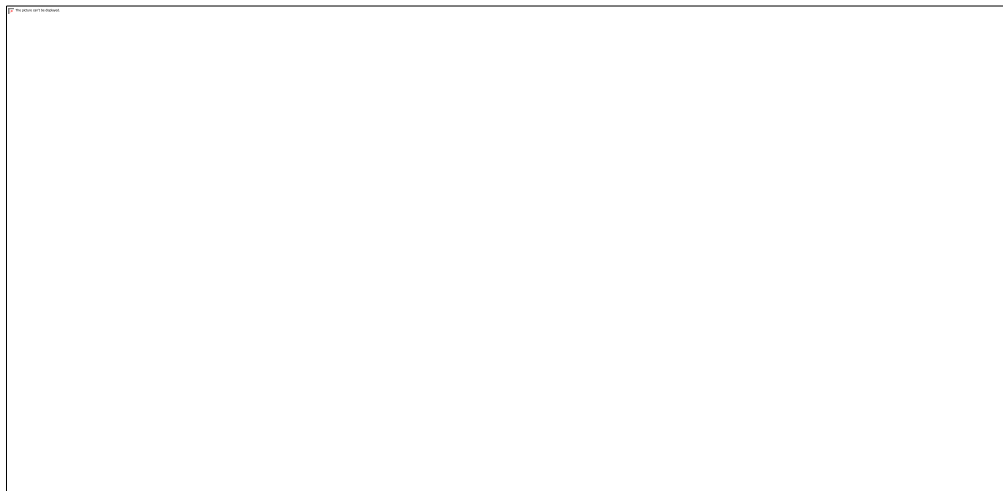


Figure 8 Schematic of AFM's basics [45].

Figure 8 show the basic AFM's set-up. A laser and a detector are used to determine the atomic force between a tip and a sample to track cantilever movement. The holder of the sample pushes the sample through a piezoelectric scanning valve up and down in order to preserve the contact force at the pre-selected stage. An image in three-dimensional can

eventually be produced when the motion of the cantilever in the Z-direction is recorded as a function of the X and Y-position of the sample [66].

2.2.4.1 Tapping, Contact, and Non-Contact Mode

Shown in Figure 9 are the AFM operation mode. The first imaging mode discovered is the contact mode and happens while the tip is continuously in contact with the surface of the sample. Meanwhile, in order to maintain the cantilever deflection stable during scanning, a feedback mechanism is normally used. This mode of operation is ideally suited to rigid surfaces and flat such as tissue, hard polymers, and crystals, allowing for the maximum degree of resolution.

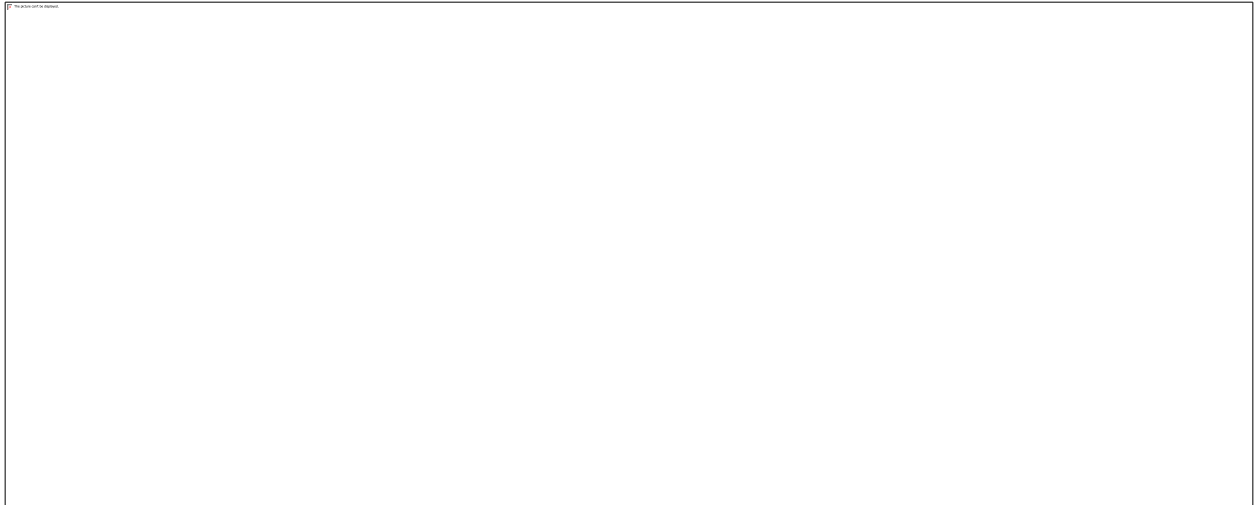


Figure 9 Tip-sample isolation curve demonstrating the major interaction during the screening of AFM with imaging modes for the regime. (B) Average roughness. (C) Root Mean Square Roughness[65].

For the Scanning of the soft materials the direct contact of the tip will easily change the sample surface with undesired damage. This can be avoided by working in non-contact mode, that is, by forcing the oscillation of the cantilever at a resonance frequency. Throughout this case, the oscillating probe affected normally by the nearest surface, thereby creating a frequency change in the resonant frequency owing to the attractive forces

of van der Waals. Finally, in the tapping mode, the tip stays oscillating with a certain resonant frequency and communicates with the sample during its oscillation. The three operating modes are summarized in Table 2 [65].

Table 2 Summary of the three operating modes in AFM measurement

Operation modes	Contact Mode	Non-contact Mode	Tapping Mode
Working Principle	The tip in contact with the surface of the sample	There is no contact between the tip and the surface of the sample	Intermittent and brief touch between the tip and the sample.
Advantage	- High resolution - High scan speeds	- No damage to the sample - Low resolution	- Minimal damage to sample - High resolution
Disadvantage	Harm to the soft sample.	The scan speed is slower as compared to the tapping mode and contact mode.	The scan speed is slower as compared to the contact mode.

2.2.5 Spectrophotometry

Spectrophotometry is a method of analyzing the intensity of light at chosen wavelengths. It used to study the optical properties of samples. This approach relies on the light-emission and/or absorbing properties of the analyte being analyzed [67]. The spectrophotometer method is used to assess light intensity as a function of wavelength. This is achieved by the diffraction of the light beam through a variety of wavelengths, the intensities are detected using a charge-coupled device, then by showing the effects as a graph on the detector and again on the display unit. The primary spectrophotometer components are a light source, monochromator, sample holder, and/or cuvette, photosensitive detector, and read-out device. The Light source: Depending on the spectrophotometric technique there are different sources of light for each one. The common sources for UV radiation are deuterium lamps and hydrogen lamps. The most prominent for visible radiation are carbon arc and tungsten filament. Where the common sources for IR-radiation are Global and Nernst Glower. Monochromator: segments the individual wavelengths into small bands after divided from the polychromatic light. The sample holder and/or Cuvette retains the sample and let the particular wavelength to flow through itself. The Cuvettes are translucent in nature and are made of quartz materials or ordinary glass. Photosensitive detector: a highly sensitive detector and capable of detecting low levels of radiant light. The read-out device: It is capable of reading the incoming signal from the detector. The spectrophotometer has the following two forms, based on the number of beams used: The first one is the single beam spectrophotometer, in this type the single beam is used to across through the sample, and with help of a reference solution, the samples can be analyzed [67].



Figure 10 Schematic diagram of a double beam spectrophotometer.

The advantage of this type it is less expensive and high sensitivity. The second one which are shown in figure 10 is the A double-beam spectrophotometer, this type used a two-beam of light, one of them passes via a test sample and offering the absorption of light from the sample, and the other across through the reference. This type provides greater detection than a single beam. If the initial intensity of light (I_0) and the intensity of transmits light (I_{tran}) through the sample are known, then the transmittance (T) can be calculated as:

$$T = \frac{I_{tran}}{I_0}$$

With the help of Beer's Law, the absorbance of light (A) can be calculated from % transmittance data.

$$A = 2 - \log_{10} \%T$$

When the absorbance, transmittance and the thickness of the sample are Known, then the optical parameters such that, refractive index and the band gap can be found[67].

2.2.6 Vibrating sample magnetometer

The vibrating sample magnetometer (VSM) is a technique pioneered by S. Foner and is used to study the magnetic properties of the materials such as saturation, hysteresis, anisotropy, and coercivity. According to Faraday's Law of induction there is an electromagnetic force produced in the coil when the flux via coil changes. If the sample is placed within a uniform magnetic field H , a magnetization M will be induced in the sample. In a vibrating sample magnetometer, the sample is placed within suitably placed sensing coils, also held at the proper angle. sample's vibrating component is mechanically vibrated in a sinusoidal motion [68].

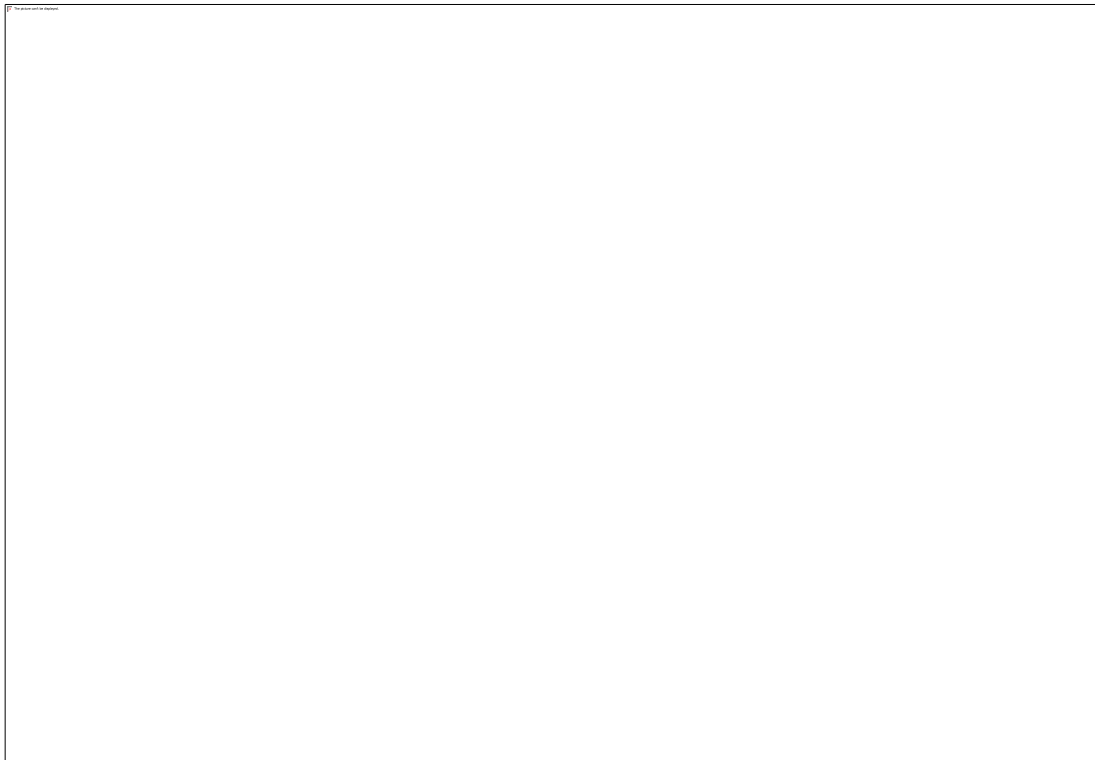


Figure 11 System representation of the VSM.

Figure above shows a schematic diagram of the apparatus VSM, there is an electromagnet to generate a magnetic field and to detect the signal there is a lock-in amplifier. The VSM has a straightforward operation. A mechanical vibrator drives a magnetic sample that is mounted on a long rod. The rod is placed in between a pole sections of an electromagnet, which has been equipped with detector coils. The magnetized sample with oscillatory motion will produce a voltage in the coils's detector, which is proportional to the magnetization of the sample. Since any change in magnetic flux allow a voltage to be induced in the sensing coils. There is a program is used to converts the changes in the signal to values in order to graph magnetization (M) versus magnetic field strength (H), which is known as a hysteresis loop[68].

CHAPTER 3

SYNTHESIS AND STUDY OF COBALT DOPED TITANIUM NITRIDE THIN FILMS

3.1 Experimental details

Cobalt doped TiN thin films were prepared by reactive magnetron co-sputtering of titanium (3N purity) and cobalt (3N5 purity) target in the presence of argon (4N purity) and nitrogen (5N purity) gasses with a flow rate of 8 standard cubic centimeter per minute (sccm) of each gas. Titanium target was sputtered by RF power that was fixed to 170 Watts for all the films whereas cobalt was sputtered by DC power and films were prepared at different DC power to control the concentration of cobalt doping in the film. The details of the growth parameters are given in table 3. Films were grown at elevated temperature of 300 °C simultaneously on fused silica and Si(001) substrates and for uniform film growth substrates were rotated at 6 rpm during the growth. Films grown on fused silica were used for optical measurements whereas films grown on Si(001) were used for all other characterizations. During the growth, the chamber pressure was kept at $2.4\text{-}3.7 \times 10^{-2}$ mbar and each film was grown for a duration of about 3 hours. Surface morphology of the films were studied using non-contact atomic force microscopy (AFM) made by Bruker diInnova

SPM. Transmission spectra of the films were acquired using JASCO V-570 double-beam spectrophotometer at the normal incidence. Chemical composition of the films was studied using x-ray photoelectron spectroscopy (XPS) by Thermo Scientific Escalab 250Xi spectrometer. XPS is performed in ultra-high vacuum, but the films are transferred in air from the growth chamber to the XPS chamber and during the deposition samples surfaces get contaminated by organic molecules in the air. To remove organic contaminants the film surface is cleaned by bombarding the surface by 2-keV Ar⁺ ion beam for 30 seconds and then full scan and high-resolution scans for titanium, cobalt, nitrogen, and oxygen were acquired. X-ray diffraction of the films were performed to study the crystallinity of the films by using a Bruker Phaser D2 x-ray diffractometer that is equipped with copper k_{α} source. Magnetic properties of the thin films were studied by the vibrating sample magnetometry (VSM) option of a DynaCool Physical Property Measurement System (PPMS) by Quantum Design, using the large bore coilset (12 mm bore) which has a 1.5×10^{-6} emu sensitivity. X-ray Reflectometry measurements were conducted on an X'Pert Panalytical Pro system, using Cu K α radiation ($\lambda=1.54$ Å). The reflectometry and fitting results were plotted in terms of the scattering vector related to the two-theta angle as $Q = \frac{4\pi}{\lambda} \sin\theta$. Quantitative fitting of the reflectometry patterns was performed using a linear least-squared method implemented in the MOTOFIT package.

Table 3 Growth conditions of cobalt doped titanium nitride samples.

Sample #	Ar (sccm)	N ₂ (sccm)	Ti-RF Power (W)	Co-DC power (W)	Growth Temp Ts (°C)	Pressure chamber (mbar)	Rotation (rpm)	Duration (Mins)
E31-M1	8	8	170	0	300	2.4-3.7x10 ⁻²	6	180
E32-M2	8	8	170	3	300	2.4-3.7x10 ⁻²	6	180
E33-M3	8	8	170	4	300	2.4-3.7x10 ⁻²	6	180
E34-M4	8	8	170	5	300	2.4-3.7x10 ⁻²	6	180
E36-M6	8	8	170	7	300	2.4-3.7x10 ⁻²	6	180

3.2 Results and discussion

3.2.1 Structural Analysis

Sample crystallinity was studied by X-ray diffraction. Shown in Figure 9 are the samples XRD pattern grown at a different percentage of cobalt. For all grown samples, the diffractogram indicates the main peaks referring to Silicon substrate, Si(002) at $2\theta = 32.8^\circ$, Si(004) at $2\theta = 61.5^\circ$, and Si(004) at $2\theta = 68.9^\circ$, and a minor peak referring to

silicon dioxide $\text{SiO}_2(100)$ at around $2\theta = 20.1^\circ$. XRD spectra of samples M1 and M2 are similar which contain four peaks at 32.8° , 61.5° , 68.9° and 20.1° , where samples M3, and M6 are very similar to the Si substrate with peaks at 32.8° , 61.5° , 68.9° . We conclude that the as-prepared thin films are amorphous.



Figure 12 XRD pattern for pure TiN and Co-TiN thin film (a) M1, (b) M2, (c) M3, (d) M4, (e) M6.

3.2.2 Optical study

Shown in Fig.13 are the transmission spectra of the films grown on the fused silica substrates. Film thicknesses are calculated using three different techniques, first of all from the transmissions spectra using the following formula [58, 69]:

$$d = \frac{\lambda_{max} \times \lambda_{min}}{4n_f|\lambda_{max}-\lambda_{min}|}$$

Where d is the thickness of the film, λ_{max} is the wavelength corresponding to a maximum in transmittance spectrum, λ_{min} is the wavelength corresponding to the adjacent minimum, and n_f is the refractive index of the film which is calculated using the empirical relation [58].

:

$$n_f = 4.22 - 2.94T_{min}$$

T_{min} is the minimum transmission.



Figure 13 The Transmission Spectra of Co-TiN Samples at different amount of cobalt.

To study the thicknesses of the amorphous TiN films, X-ray reflectometry experiments were conducted and the available results are included in Table 4. A representative dataset is shown in Fig. 14 along with the scattering model determined by fitting. Below a critical Q-value in the data (proportional to the angle), total external reflection occurs such that the normalized reflectivity R approaches unity, whereas at higher Q, the reflectivity falls off and shows periodic Kiessig fringes caused by the interference pattern of the X-rays

reflected at various film interfaces. From the periodic spacing of the Kiessig fringes at higher Q , the thickness of the oxynitride layer can be determined by fitting a model scattering length density profile (SLD) to the data. All films studied had thicknesses in the range from 63 – 76 nm. Figure 14b shows the best fitted model for M2. To fit the XRR, a model was developed of a three-sub-layer film on top of a silicon substrate, consisting of a water absorbate region, a thin surface oxide and a bulk $\text{Ti}_y(\text{N}_{1-x}\text{O}_x)$ region. The majority of the layer is made up by a uniform cobalt-doped $\text{Ti}_y(\text{N}_{1-x}\text{O}_x)$ film which has an X-ray SLD of $32 \times 10^{-6} \text{ \AA}^{-2}$. This implies that the film has oxidized uniformly through its bulk, similar to past reports where this bulk oxidation was noted after exposing the substoichiometric TiN_x starting material to the air over a duration of several hours [70]. Near the surface, additional complexity occurs, owing to the formation of a thin (1.5 – 4 nm) TiO_2 overlayer. The latter appears to be the intrinsic native oxide that forms on TiN films. Finally, on top of the TiO_2 appears a thin layer of a third material with a low SLD values and a thickness of (2-3 nm). This may be a low-density region of the oxide, but it is tentatively identified as a thin H_2O water absorbed layer based on the observed SLD value ($9.4 \times 10^{-6} \text{ \AA}^{-2}$) which matches that of H_2O layers known to form on TiO_2 . Despite the small variations in the top 3-4 nm of the film surface, these results show that the optical and magnetic properties of the films will be primarily determined by the thick uniformly cobalt-doped oxynitride region below the surface, as this makes up the majority of the film volume.

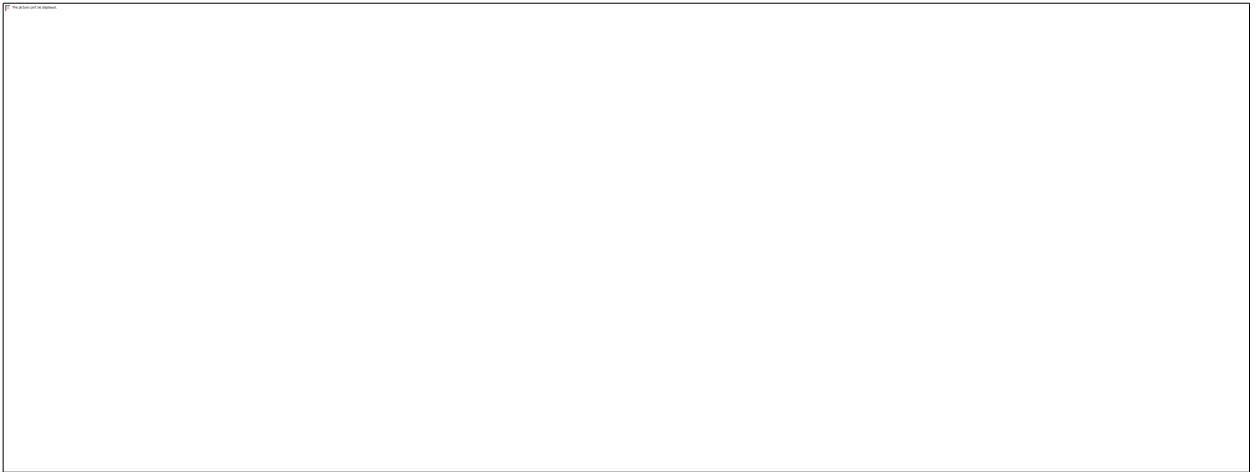


Figure 14 (a) X-ray reflectivity of sample M2. The points are the data and the solid line is the best fit to the data. (b) The fitted X-ray scattering length-density profile shows the three sub-layers that comprise the film structure.

Film thicknesses are calculated using SEM. Fig. 15 shows the thickness of the Co-TiN films collected by the top-view and cross-section of the SEM images. The thickness of the films is found to be between 96 nm and 118 nm. We took the average for all these thickness measurements and used them to calculate the bandgap of the films.



Figure 15 Cross-section images of Co-TiN films deposited at different DC power for cobalt using SEM. (a) M1, (b) M2, (c) M3, (d) M4, (e) M6.

The optical band gap of the films was obtained by using the following relation [56, 58, 69]:

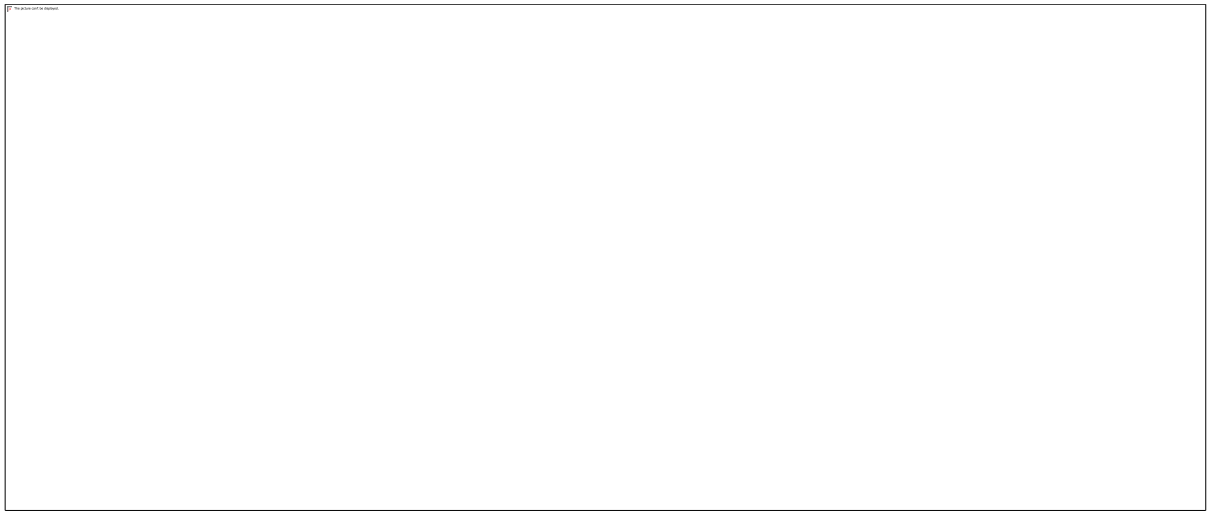
$$(\alpha E)^2 = \beta(E - E_g)$$

where α is the absorption coefficient, E is the incident beam photon energy, β is a constant and E_g is the bandgap of the film. Shown in Fig. 16 are the plots of $(\alpha E)^2$ as a function of incident photon energy E , these plots are typically called Tauc plots. By extrapolating the linear portion of the plot to the horizontal axis the bandgap of the film is obtained. The bandgap values of the films are given in Table 4 with the thickness measurements. The bandgap values decrease with the increase in cobalt concentration in the film, which is due to cobalt dopants forming shallow donor states in the bandgap and hence transition from valence band to the donor states would result in smaller measured bandgap. Similar effect of red-shift in the bandgap was reported for cobalt doped ZnO due to the sp-d exchange between electrons of the ZnO band and localized d-electrons associated with Co^{+2} has been reported [46, 71-75].



Figure 16 Tauc plot of undoped and doped TiN grown films.

Table 4 Thickness and band gap of Co-TiN films.



3.2.3 Surface Morphology

Atomic force microscopy is used to study the surface morphology of the undoped/Cobalt-doped titanium nitride grown films. Shown in Fig. 16-21 are the two and three-dimensional AFM images with size $2 \times 2 \mu m^2$ of undoped /Co-TiN films. All the films have grainy surface structure and there is little change in the surface morphology of the films with the change in cobalt concentration in the films. Root mean square (RMS) surface roughness and the average grain size, as estimated by AFM images using Gwyddion software, are given in table.5[76]. Grain size were estimated by using mark grains by edge detection option and setting the Laplacian threshold to a value which would results in maximum

number of grains. There is little effect of cobalt concentration on the grain size of Co-TiN films, but RMS surface roughness increases slightly with the increase in cobalt concentration. All doped TiN films is found to have RMS roughness higher than undoped TiN films. Sample E31 is the control sample of pure TiN with no cobalt doping. This indicates that cobalt is catalyzing the process of film formation which are observed in other measurement.

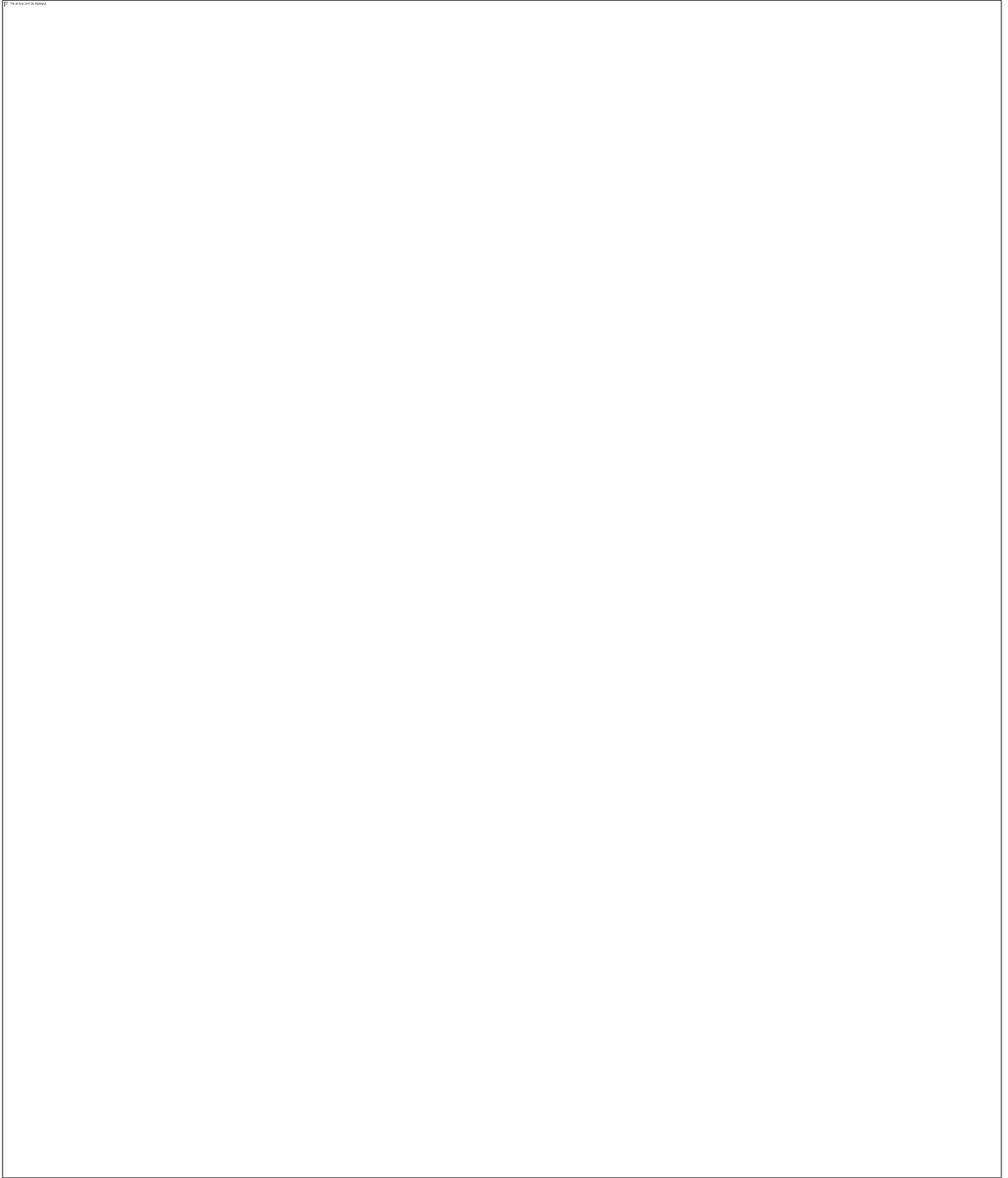


Figure 17 AFM images with size $2 \times 2 \mu\text{m}^2$ of undoped-TiN films.(a) Two- dimensional, (b) three-dimensional.

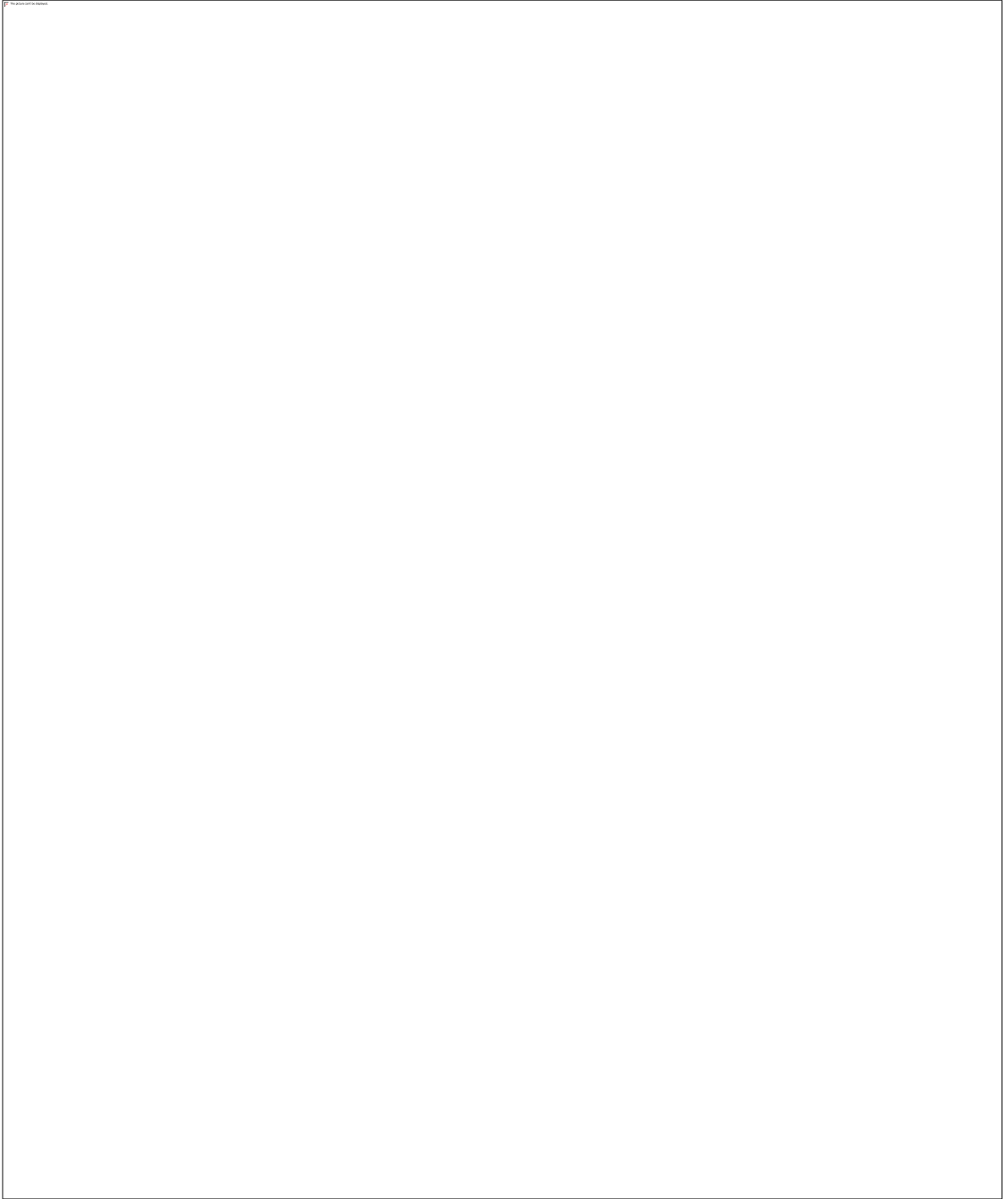


Figure 18 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M2.(a) Two- dimensional, (b) three-dimensional.

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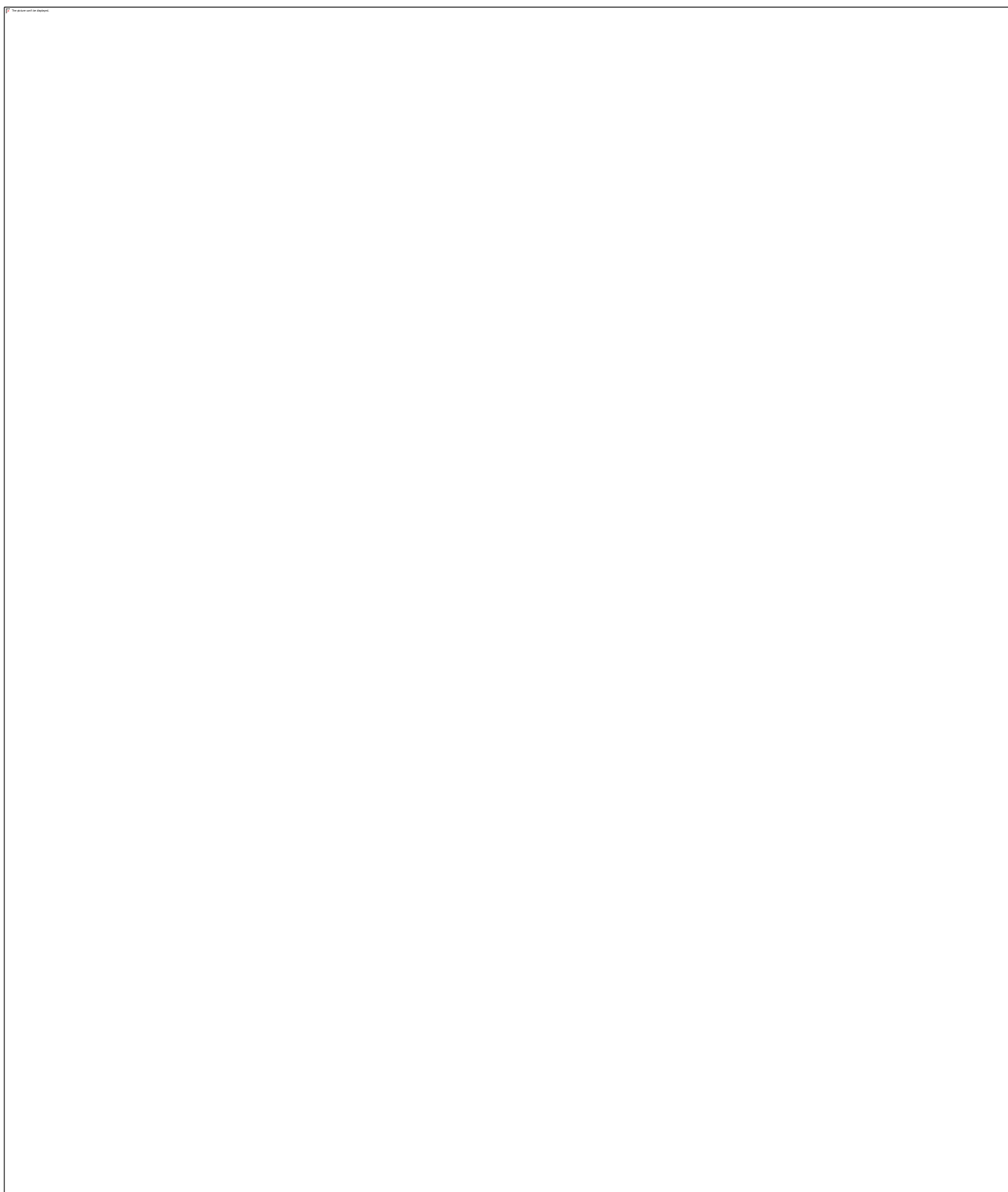


Figure 19 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M3.(a) Two- dimensional, (b) three-dimensional.

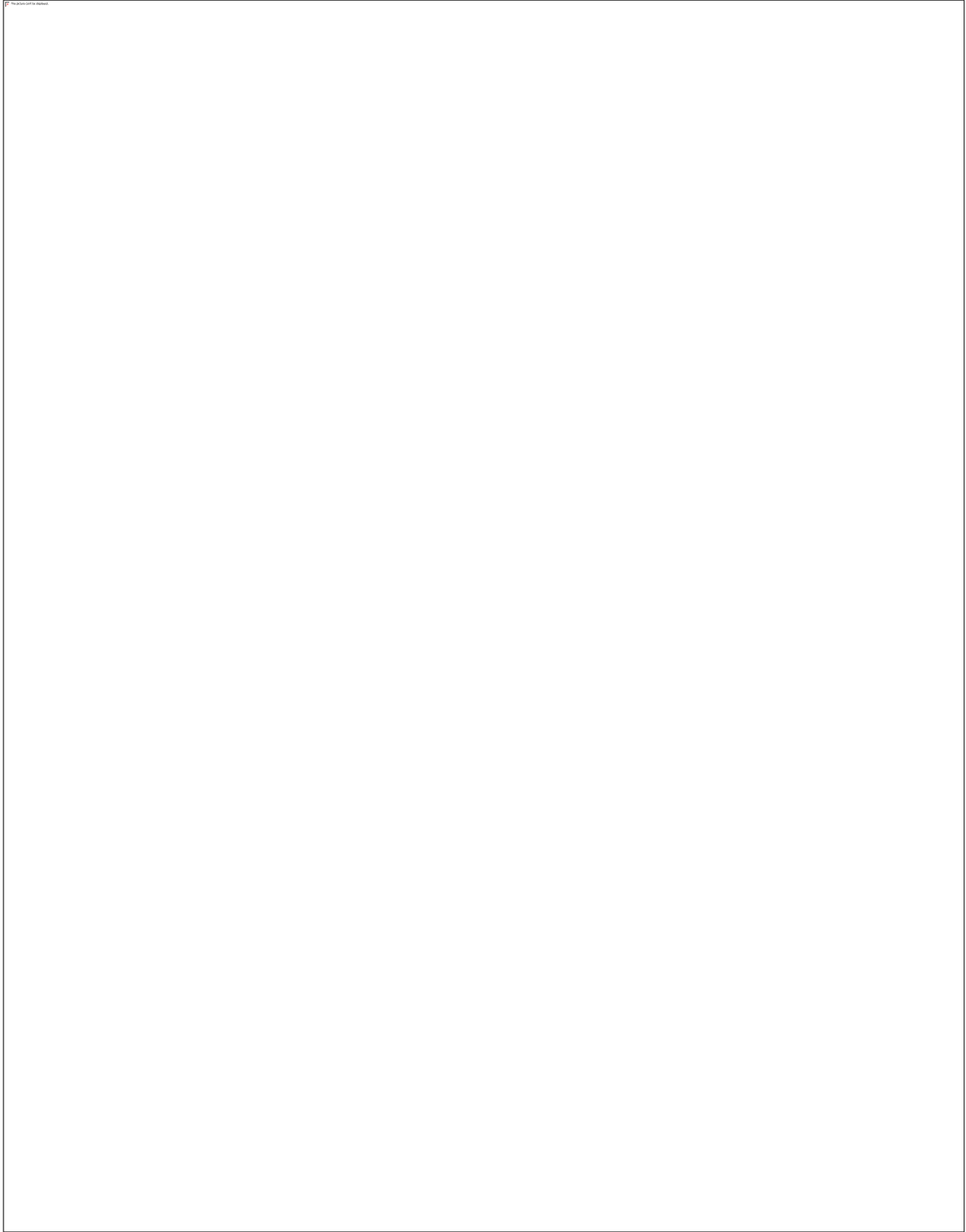


Figure 20 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M4.(a) Two- dimensional, (b) three-dimensional.



Figure 21 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M6.(a) Two- dimensional, (b) three-dimensional.

Table 5 Average surface RMS roughness and average grain size as measured by AFM.

Sample#	Average Surface RMS roughness (nm)	Average Grain size estimated by AFM (nm)
E31-M1	0.4 ± 0.04	6.1 ± 0.1
E32-M2	0.5 ± 0.14	9.2 ± 0.6
E33-M3	0.7 ± 0.10	9.2 ± 1.0
E34-M4	1.7 ± 0.17	6.3 ± 0.6
E36-M6	1.1 ± 0.04	8.1 ± 0.1

3.2.4 XPS study

Shown in Figure 22 are the full scan XPS spectra of TiN and Co-TiN films indicating the presence of several elements in the film. Both spectra contain XPS peaks of C1s, Ar2p, N1s, Ti2p, and O1s along with Auger peaks of these elements. Co-TiN spectrum has a Co2p peak which is not present in TiN spectrum. After the film growth, samples were exposed to air before transferring to the XPS chamber, which resulted in oxidation of the films. For this reason, a prominent oxygen peak is present in the XPS spectra of all of our films. The presence of C1s peak was due to organic contamination of the sample when exposed to atmosphere and C1s peak at 284.8 eV was used as a reference peak to correct the data for any shift in the spectrum due to any charging effect. After the first scan, the film surface was etched by bombarding the surface with 2keV Ar⁺ beam for 30 seconds to remove organic contaminants. The presence of Ar2p peak in the XPS spectra could be due to the use of argon ions for etching of the film.

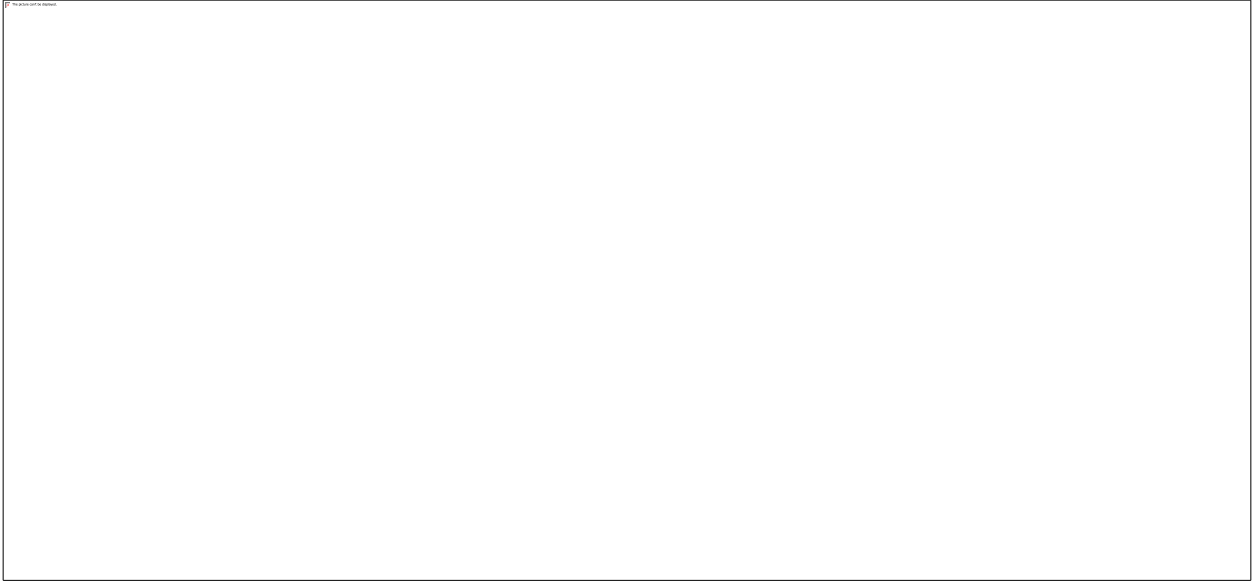


Figure 22 Full scan XPS survey spectra of TiN film (M1) and Co-TiN films (M6).

Shown in Figure 23(a) is the high resolution XPS spectra of $Ti2p_{3/2}$, with their deconvoluted peaks for samples M6 whereas Figure 23(b) is $Ti2p_{3/2}$, spectra of all samples overlaid on each other. XPS spectra of $Ti2p$ is split into two peaks $Ti2p_{3/2}$, $Ti2p_{1/2}$, due to spin-orbit coupling. Shown in Figure 23(a) is $Ti2p_{3/2}$ peak, which appears as a broad peak so by peak fitting analysis it was deconvoluted into three peaks centered at 456.2 eV, 457.5 eV, and 459.3 eV that corresponds to titanium nitride (TiN), titanium oxynitride (TiO_xN_y), and titanium dioxide (TiO_2) respectively [58, 77, 78]. The presence of TiO_2 related XPS peak is due to exposure of the film to the atmosphere before transferring to the XPS chamber.

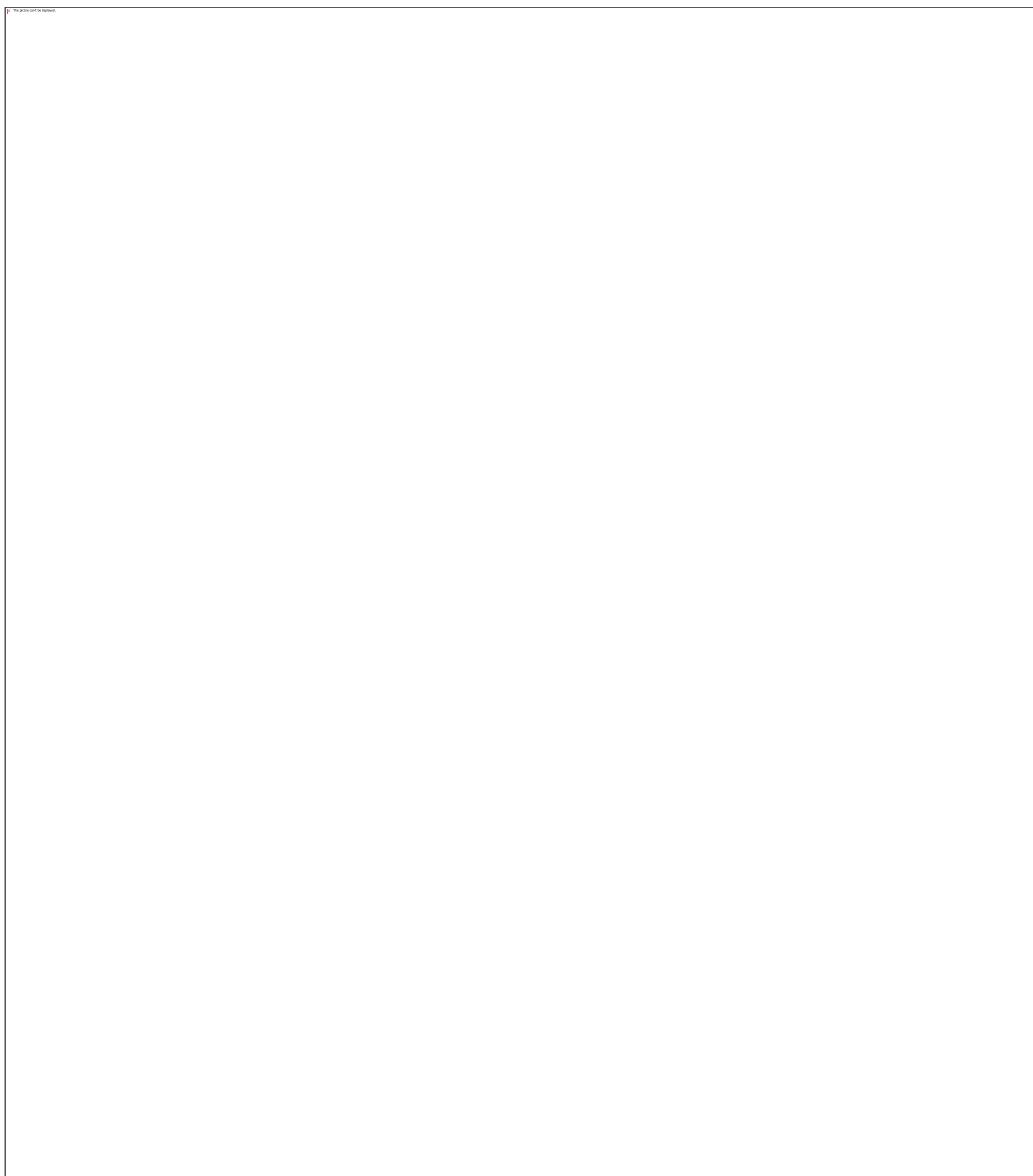


Figure 23 High resolution XPS spectra of (a) Ti2p_{3/2} for sample M6 with its deconvoluted peaks, (b) Ti2p_{3/2} for all the samples.

It was observed that intensity of TiO₂ related XPS Ti2p_{3/2} peak was higher compared to Ti2p_{3/2} peaks due to TiN and TiO_xN_y in low cobalt doped films but as the cobalt concentration increases in the films the intensity of Ti2p_{3/2} peak due to TiN increases compared to the intensity of Ti2p_{3/2} peak due to TiO₂ as shown in Figure 23(b) and Figure

24. This indicates that cobalt enhances the nitridation of the film.

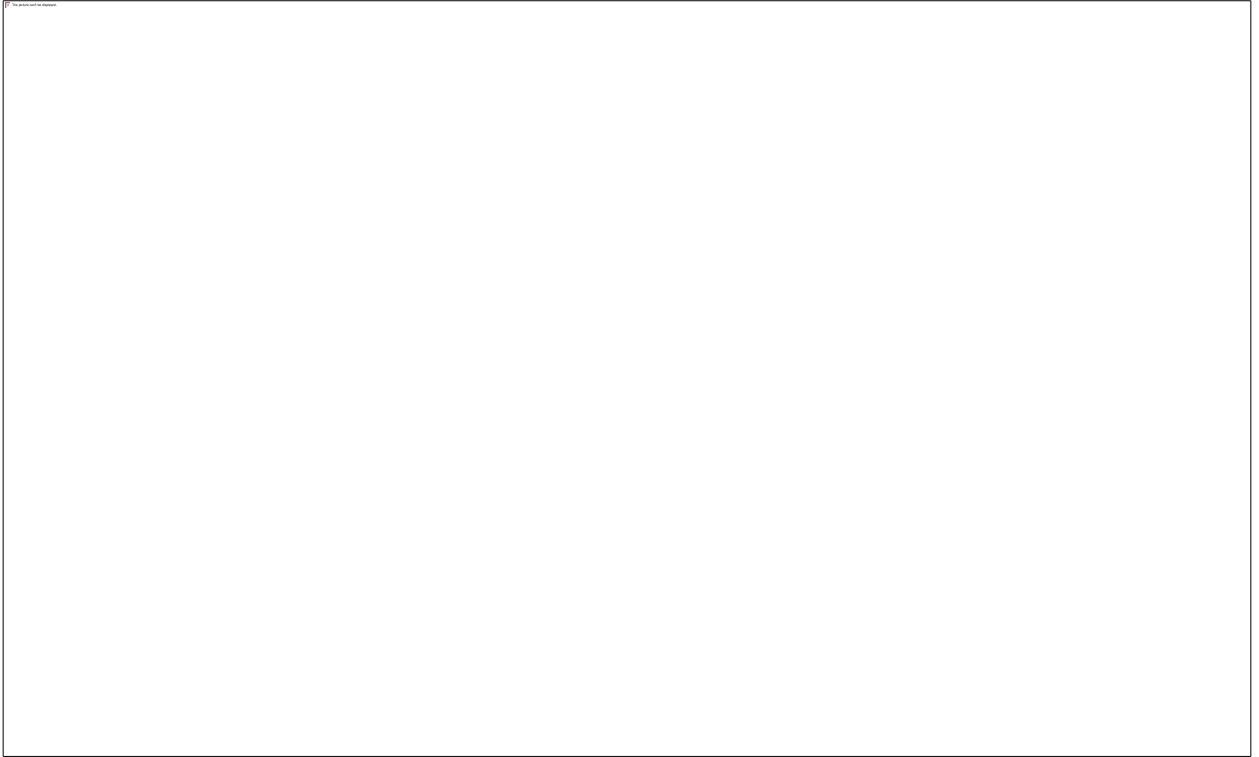


Figure 24 High resolution XPS Ti2p_{3/2} spectra for the grown thin films with their deconvoluted peaks. (a) M1, (b) M2, (c) M3, (d) M4.

Given in table.6 are the peaks positions of Ti2p_{3/2} for all the samples which indicate that all the samples have peaks due to TiN, TiO_xN_y and TiO₂. Figure 24 is Ti2p_{3/2}, spectra of all other samples with their deconvoluted peaks.

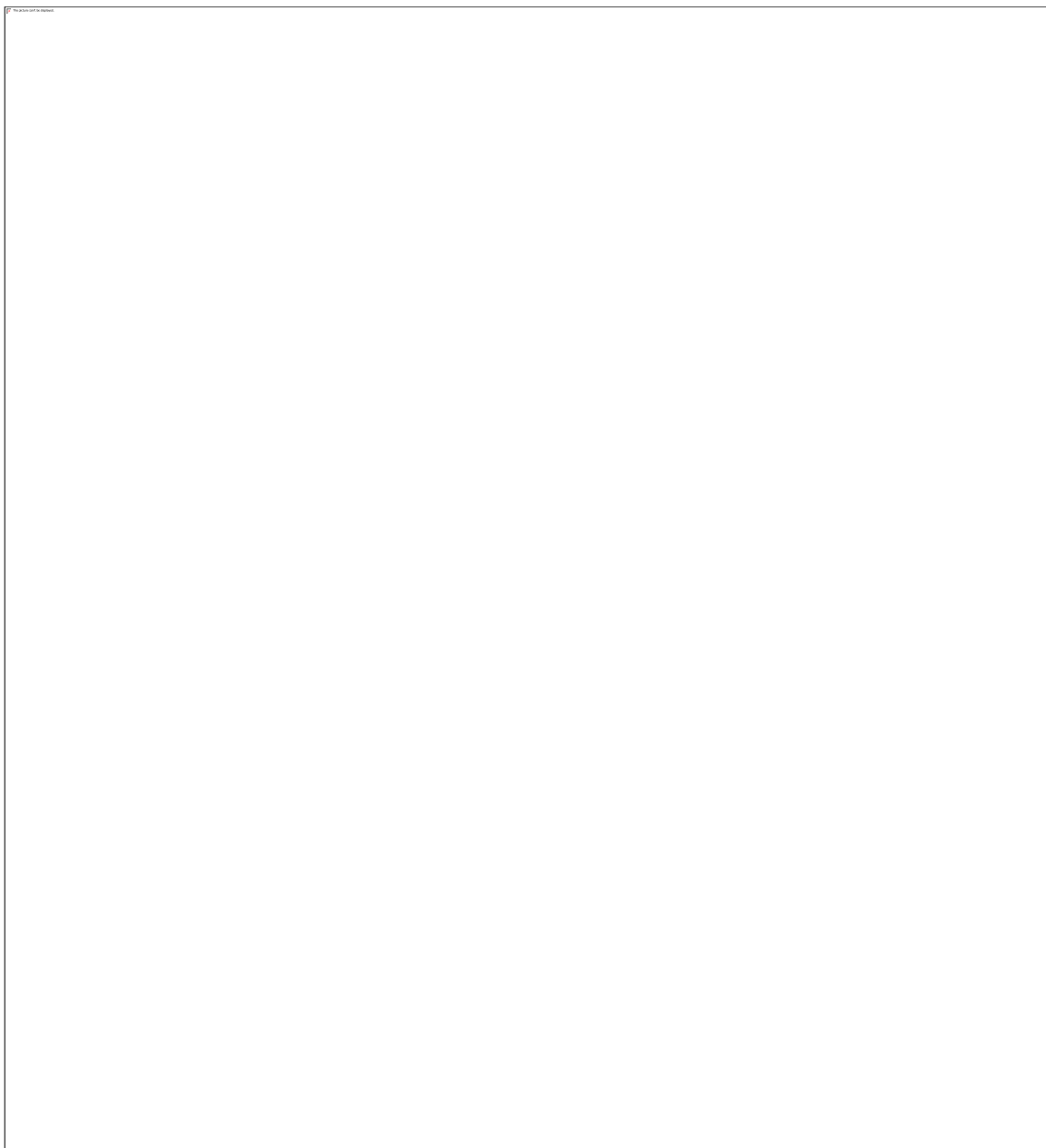


Figure 25 High resolution XPS spectra of (a) N1s for sample M6 with its deconvoluted peaks, (b) N1s for all the samples.

Shown in Figure 25(a) is N1s spectrum of sample M6 and using peak fitting analysis N1s peak could be deconvoluted into two peaks centered at 397.7 eV and 398.9 eV, whereas Figure 25(b) is N1s spectra of all samples overlaid on each other. The major peak found at 397.7 corresponding to TiN and the second peak centered at 398.9 is related to TiO_xN_y [57, 79]. Figure 26 is N1s spectra of all other samples with their deconvoluted peaks.

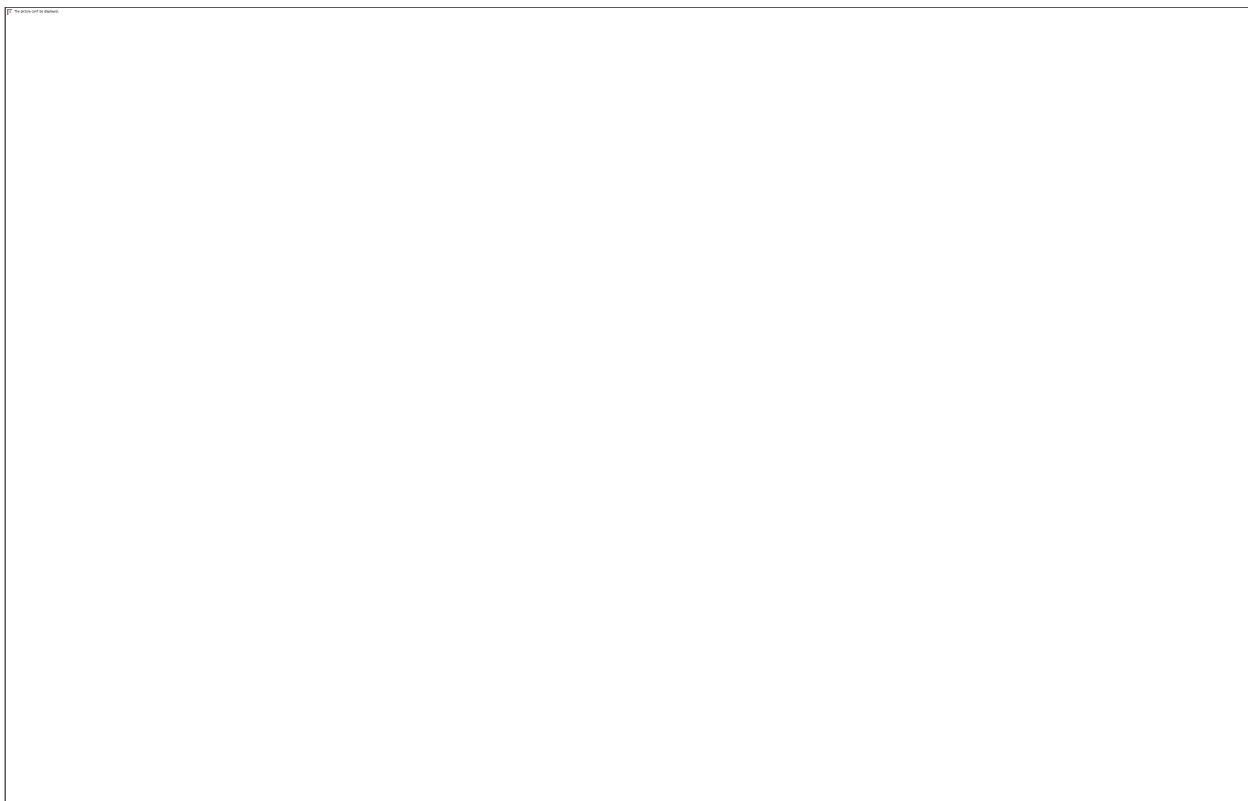
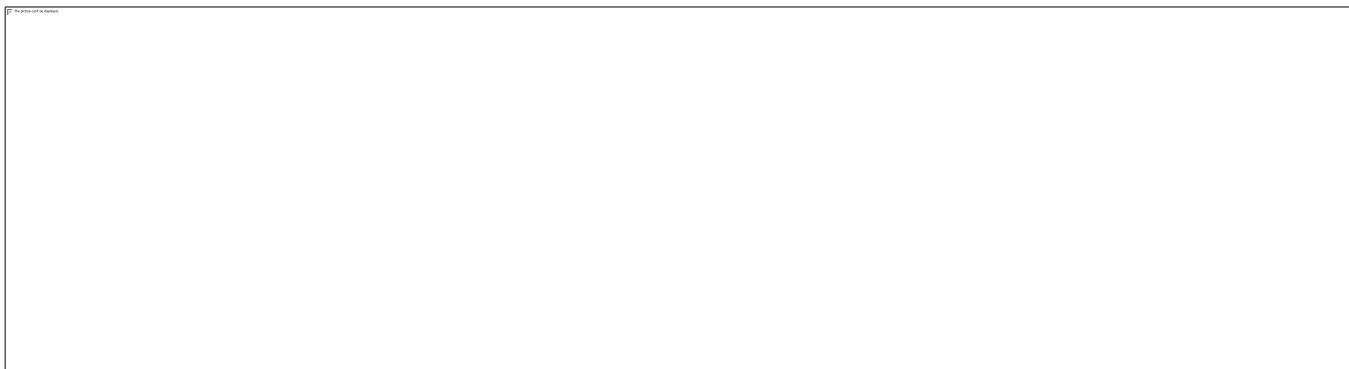


Figure 26 High resolution XPS N1s spectra for the grown thin films with their deconvoluted peaks. (a) M1, (b) M2, (c) M3, (d) M4.

Table 6 XPS peak positions of Ti2p_{3/2}, N1s, and Co2p_{3/2} for all the samples (All values are in eV)



Shown in Figure 27(a) is the high resolution XPS spectra of Co2p_{3/2}, with their deconvoluted peaks for samples M6 and Figure 27(b) is Co2p_{3/2}, spectra of all samples overlaid on each other. Due to spin-orbit coupling the XPS spectra of Co2p is split into two peaks Co2p_{3/2}, Co2p_{1/2}. The Co2p_{3/2} spectrum for sample M6 by peak fitting analysis was

deconvoluted into three peaks with binding energies centered on 779.9 eV, 783.7 eV, and 788.6 eV. Since there is no $\text{Co}2p_{3/2}$ peak centered on 778eV which is due to metallic cobalt so cobalt in our films either bonded with nitrogen or oxygen [80].

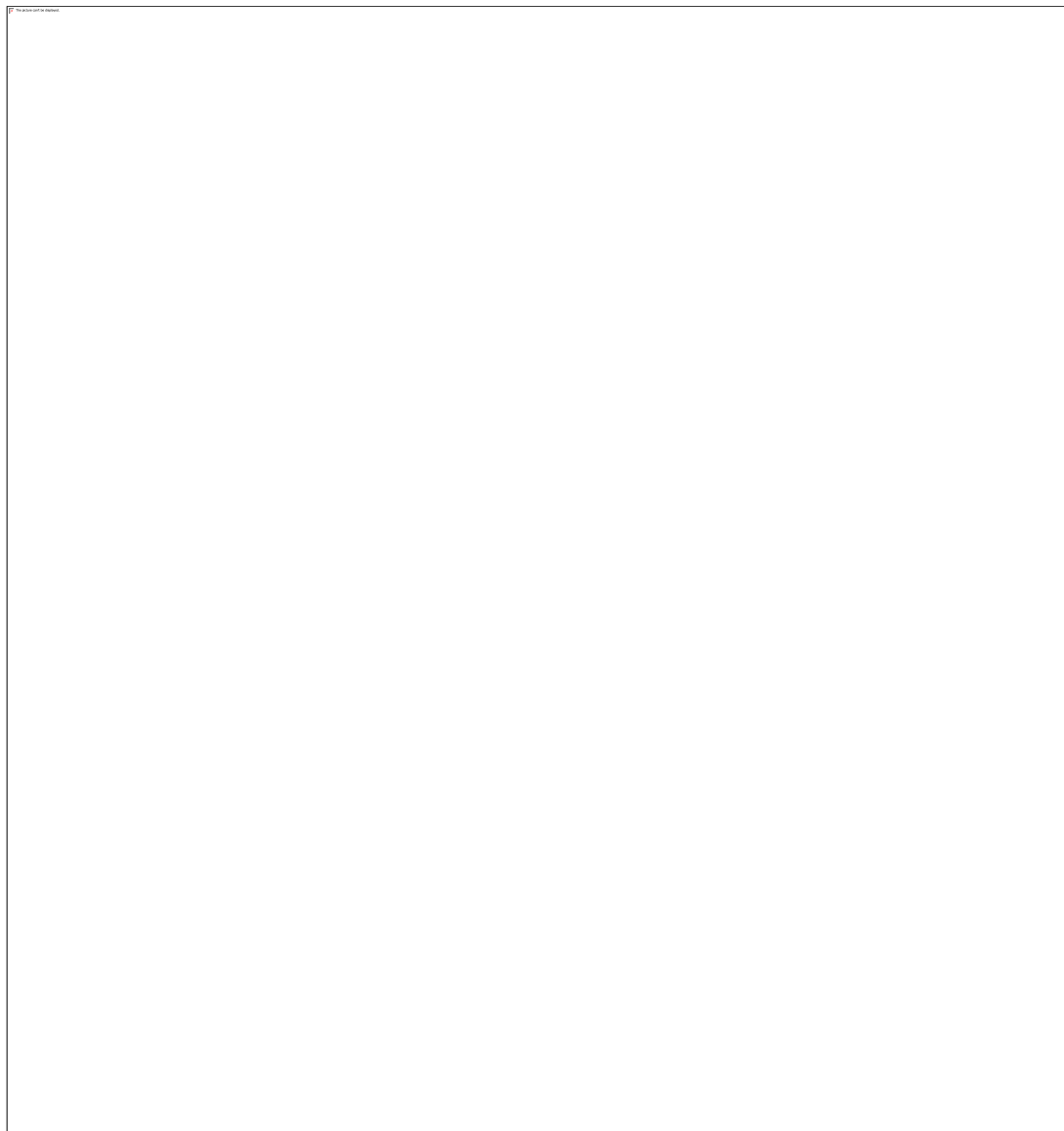


Figure 27 High resolution XPS spectra of (a) $\text{Co}2p_{3/2}$ for sample M6 with its deconvoluted peaks, (b) $\text{Co}2p_{3/2}$ for all the samples.

The difference in energy spacing between $\text{Co}2p_{3/2}$ and $\text{Co}2p_{1/2}$ of the first peak at 779.9 eV is around ~15 eV and for the second peak at 783.7 eV the difference in energies of the spin split peaks (ΔE) is around ~16 eV, which indicates that the first peak at 779.9 eV is due to

Co⁺³ and the peak at 783.7 eV is due to Co⁺² [81]. The values of ΔE for Co⁺³ and Co⁺² peaks are given in table.6. Co2p_{3/2} peak at 788.6eV is a shake-up satellite peak which is always present for Co⁺² and is absent for low spin Co⁺³ which indicates that our samples contain cobalt in both low spin Co⁺³ and high spin Co⁺² [82-84]. Since the peak intensity of low spin octahedrally bonded Co⁺³ related Co2p_{3/2} peak compared to the respective high spin Co⁺² tetrahedral peak, which indicates that most of the cobalt is in low spin state with S=0. The Co2p_{3/2} spectra of all other samples with their deconvoluted peaks is shown in Figure 28.

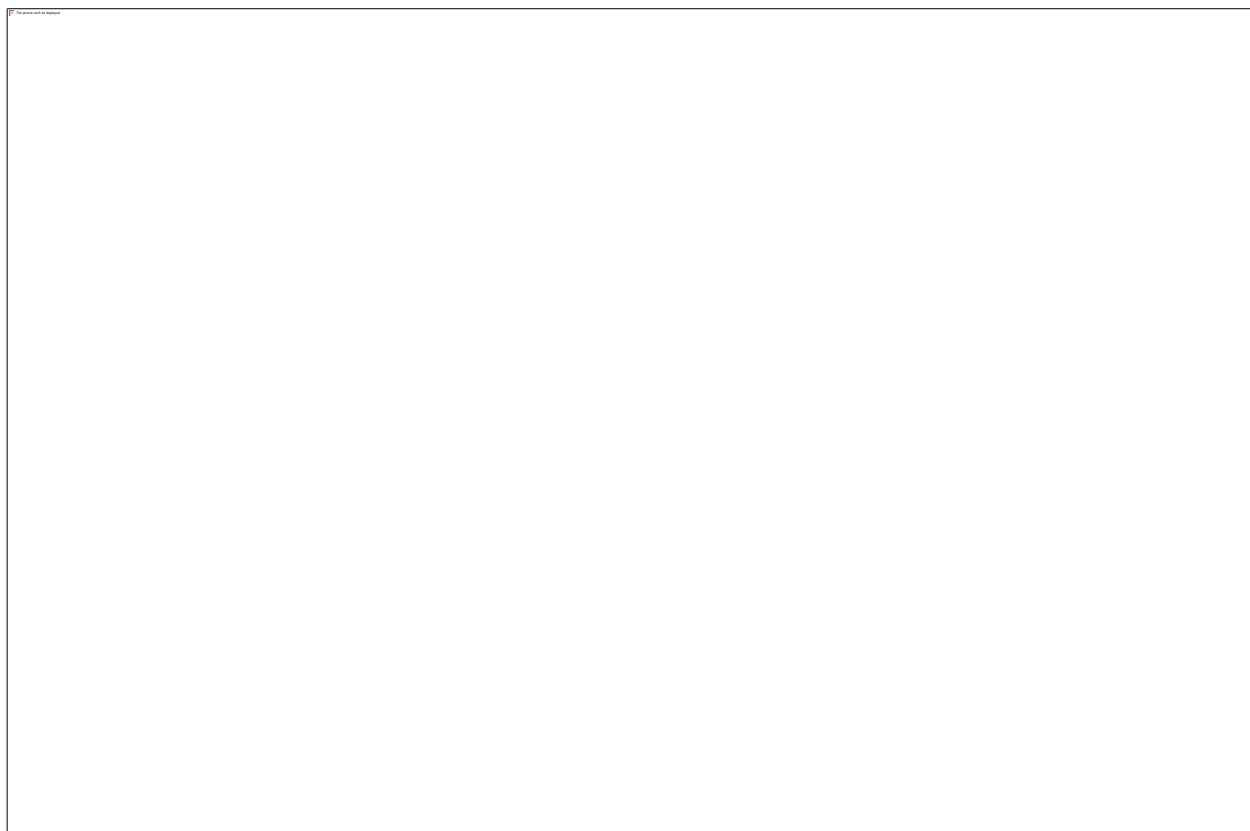


Figure 28 High resolution XPS Co2p_{3/2} spectra for the grown thin films with their deconvoluted peaks. (a) M2, (b) M3, (c) M4.

Similarly, high-resolution XPS spectra of O1s are shown in Figure 29(a) with their deconvoluted peaks for samples M6 where shown in Figure 29(b) are the XPS spectra of

O1s of all the films overlaid on top of each other. O1s spectra can be deconvoluted into two peaks centered on 531.4 eV and 532.6eV. The first peak is corresponding to TiN_xO_y and the peak centered at 532.6eV is due to O-H which is due to moisture deposited in the film when the samples were exposed to air. Similar peak fitting was performed for all other samples and shown in Figure 30[85].

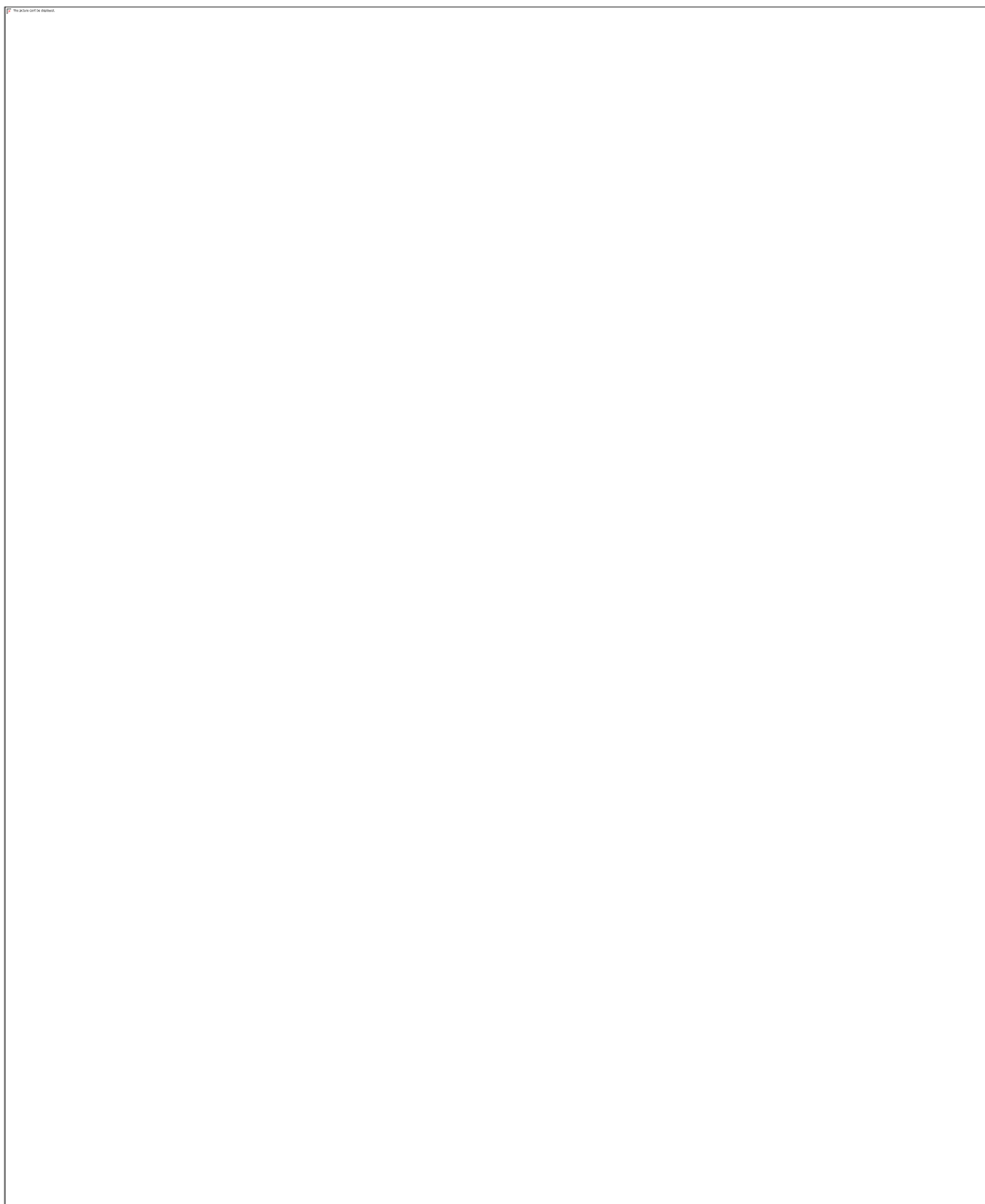


Figure 29 High resolution XPS spectra of (a) O1s for sample E36 with its deconvoluted peaks, (b) O1s for all the samples.

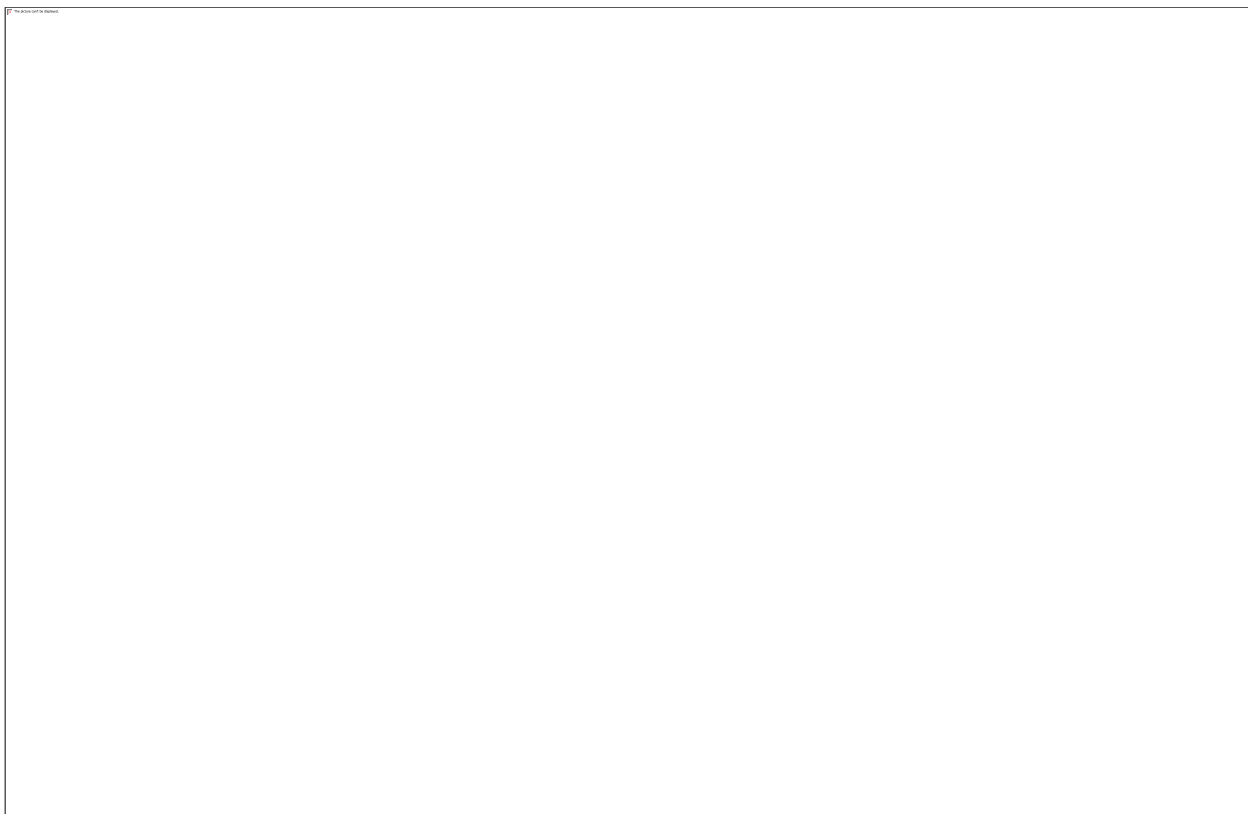


Figure 30 high resolution XPS O1s spectra of Co-TiN thin films with their deconvoluted peaks. (a) M1, (b) M2, (c) M3, (d) M4.

3.2.5 Magnetic characterization

To characterize the magnetic properties, hysteresis loops were measured from the base cryogenic temperatures (3-5 K) to room temperature. Figure 31 shows the data for M3, M4 and M6 which are samples with increasing atomic percentages of cobalt as summarized in Table 3. The inset in each figure shows the raw data for each film, which is dominated overall by a strong linear negative diamagnetic (DM) contribution at high fields but shows some non-linear regions at low fields.

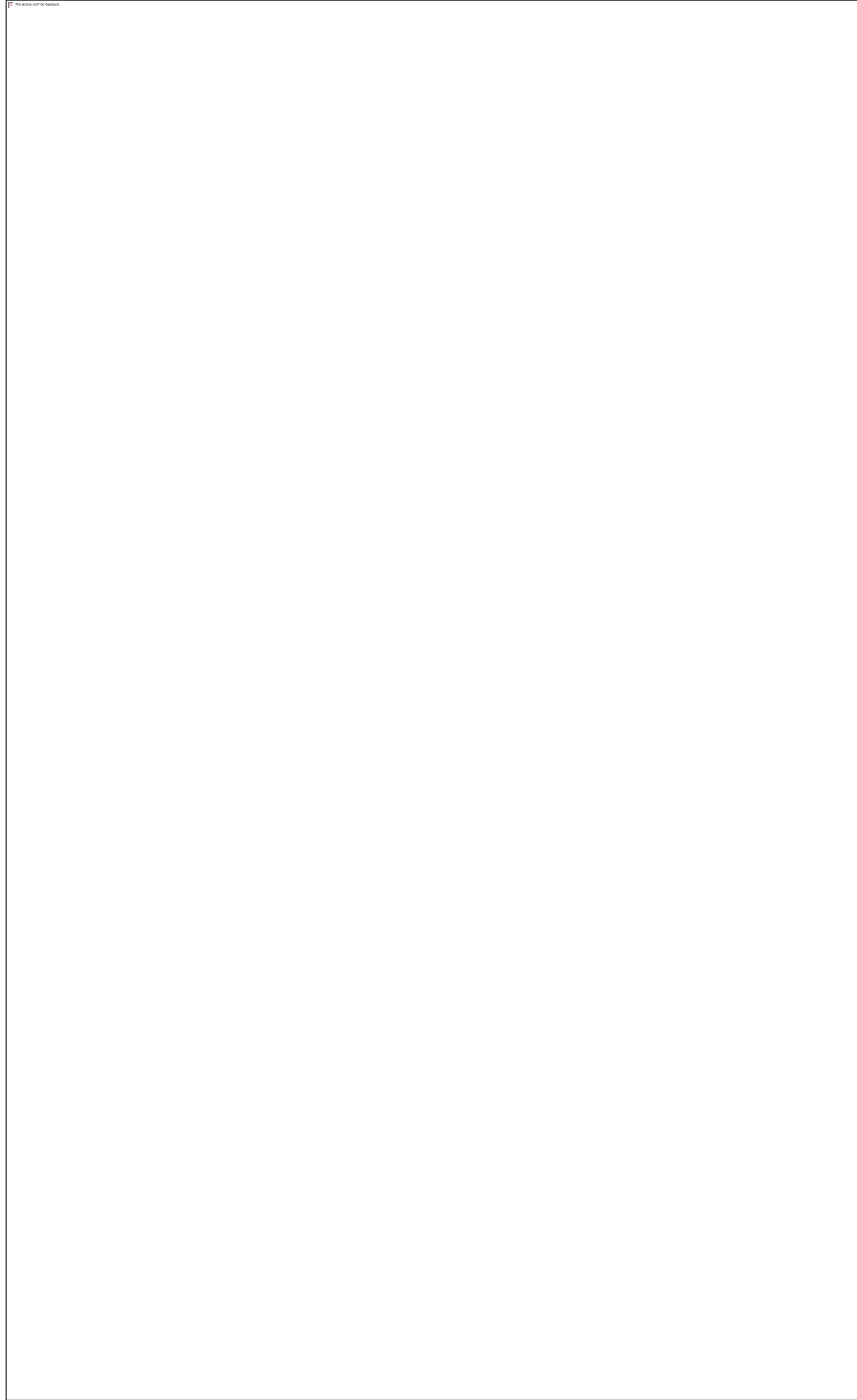


Figure 31 Magnetic field versus magnetic moment for (a) sample M3, (b) sample M4, (c) sample M6 at base temperature (3-5 K) and room temperature 300 K after subtraction of diamagnetic contribution of the substrate.

The negative slope at higher fields is attributed to the silicon substrate contribution, whereas the non-linear regions at low fields originate from the cobalt-doped film. As is common practice, the DM signal was assumed to be temperature independent and subtracted to emphasize the smaller underlying film signal which is temperature-dependent. After subtraction, samples M3, M4 and M6 all show a small positive, non-linear hysteresis loop below 5000 Oe, attributed to the contribution from the cobalt spins and other magnetic defects in the TiN films. The left-axis is the raw recorded magnetization which is in the ~ 10 micro emu range, providing a signal that is weak, but still readily detectable above the background of the instrument. The magnetization was scaled by the film thickness and measured area and expressed in terms of emu/cm^3 as labelled on the right-hand axis. For the most lightly doped sample, M3, the magnetization is negligibly small $< 0.2 \text{ emu}/\text{cm}^3$ and the signal is almost temperature independent. Defects (e.g. N or O vacancies, trapped electrons) may contribute to this very weak magnetism, as the associated “ d^0 ” magnetic phenomena are often temperature-independent [86]. However, for the samples containing higher concentrations of cobalt in Figure 31b and 31c there is much larger, temperature-dependent magnetization, that increases at low temperature. This indicates that cobalt doping enhances the magnetic properties in the samples. In both cases, however, as the magnetization passes through zero, as the field approaches zero. Whereas a “square-shaped” hysteresis loop is the signature of an ideal ferromagnet, an S-shape loop, and lack of a coercive field is generally a hallmark of paramagnetic or superparamagnetic systems. For sample M4, the response is clearly paramagnetic, because the response is strongly temperature-dependent, and the S-shaped loop occurs over a high field range. The peak magnetization in M4 approaches thick $4.3 \text{ emu}/\text{cm}^3$. For comparison, the maximum

magnetization reported in Co:TiO₂ varies in the range of 10 - 250 emu/cm³, with a complex dependency on the doping level [87, 88]. The magnetization in sample M6 in Figure 32c is slightly lower than that of M4, with 1.8 emu/cm³. Furthermore, in M6, the non-linear region occurs at lower fields which indicates modified exchange interactions or anisotropy in the more heavily doped sample. The modified magnetic properties are suggestive of a mixture of superparamagnetism and paramagnetism that varies with the cobalt concentrations. The type of magnetic hysteresis observed for the cobalt-doped oxynitride is commonly encountered in the field of dilute magnetic semiconductors, and its origin remains debated. It was proposed the lack of a coercive field is due to a wandering anisotropy axis which coexists with magnetic order [89]. The alternate proposal is that this is a signature of superparamagnetism caused by clustering of the magnetic species to form small isolated ferromagnetic particles embedded in the semiconductor which only form short-range or paramagnetic order but do exhibit some form of anomalous interparticle coupling. We note that the hysteresis loops measured for the cobalt doped oxynitride films are similar to Fe-doped TiN and Mn-doped TiN reported in past literature [56], neither of which exhibit a significant coercive field. Furthermore, the non-monotonic relationship between the magnetization and doping suggests a complex magnetism where nitrogen vacancies and other defects may be critically important to the magnetic state in titanium oxynitrides, as reported in the oxide and nitride parent structures [86, 90].

CHAPTER 4

SYNTHESIS AND STUDY OF CHROMIUM DOPED TITANIUM NITRIDE THIN FILMS

4.1 Experimental details

Chromium doped TiN (Cr-TiN) thin films were grown on Si (001) and fused silica substrates at 300 °C by sputtering Titanium (99.9% purity) and chromium (99.95% purity) targets simultaneously using RF and DC powered sputtering guns respectively. Sputtering was performed in the presence of argon (99.99% purity) and nitrogen (99.999% purity) gasses with a flow rate of 8sccm (standard cubic centimeter per minute) for both. Titanium sputtering power was fixed for all the films but DC sputtering power for chromium was varied to control the concentration of chromium doping in the film. The growth parameters of Cr-TiN films are given in Table 7. During the growth, the substrate was rotated at 6 RPM to achieve uniform film. The deposition time was 3 hours. Prior to placing the substrates in the growth chamber, they were chemically cleaned by sonicating them first in acetone and then in isopropanol for five minutes in each solvent. The chamber was evacuated to a pressure of about $1 - 3 \times 10^{-7}$ Torr before placing the start of the growth. After the growth, samples were taken out of the chamber and transmittance measurements of the grown films were carried out using a JASCO V-570 double-beam spectrophotometer in the range of 200-2000 nm at the normal incidence. Transmittance spectra was used to measure the bandgap of the films as well as to calculate the thickness of the films. Surface morphologies of the films were studied by atomic force microscopy (AFM) using non-

contact mode AFM, Bruker diInnova SPM. Chemical composition of the films was studied by x-ray photoelectron spectroscopy (XPS) by Thermo Scientific Escalab 250Xi spectrometer. The film's surface was etched for 30 seconds via 2-keV Ar⁺ ion beam to remove organic contaminants that deposit during the transfer of the sample from the growth chamber to the XPS chamber. XRD measurements were performed using Bruker's D2 Phaser diffractometer. Magnetic properties of the thin films were studied by the vibrating sample magnetometry (VSM) option of a DynaCool Physical Property Measurement System (PPMS) by Quantum Design, using the large bore coilset (12 mm bore) which has a 1.5x10⁻⁶ emu sensitivity. X-ray Reflectometry measurements were conducted on an X'Pert Panalytical Pro system, using Cu K α radiation ($\lambda=1.54$ Å). The reflectometry and fitting results were plotted in terms of the scattering vector related to the two-theta angle as $Q = \frac{4\pi}{\lambda}\sin\theta$. Quantitative fitting of the reflectometry patterns was performed using a linear least-squared method implemented in the MOTOFIT package.

Table 7 Growth conditions of Chromium doped titanium nitride samples.

Sample#	Ar(Sccm)	N ₂ (Sccm)	Ti-RF Power (W)	Cr-Dc power (W)	Growth Temp: Ts(°C)	Pressure chamber (mbar)	Rotation (Rpm)	Duration (Mins)
E31-M1	8	8	170	0	300	2.4-3.7x10 ⁻²	6	180
E38-M7	8	8	170	3	300	2.4-3.7x10 ⁻²	6	180
E39-M8	8	8	170	4	300	2.4-3.7x10 ⁻²	6	180
E40-M9	8	8	170	5	300	2.4-3.7x10 ⁻²	6	180

E42-M10	8	8	170	7	300	2.4- 3.7x10 ⁻²	6	180
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4.2 Results and discussion

4.2.1 Structural Analysis

XRD measurements were performed using Bruker's D2 Phaser diffractometer. Shown in Figure 32 is the XRD analysis of the Cr-TiN thin films grown at different concentrations of Chromium. A closer look at the XRD patterns reveals that Cr-TiN grown thin films are amorphous. The XRD results shows four peaks located at $2\theta = 32.8^\circ$, 61.5° , 68.9° come from the silicone substrate oriented in the direction (002), (320), and (004) respectively and peaks around $2\theta = 20.1^\circ$ come from SiO_2 oriented in the direction (100).



Figure 32 XRD scan of pure TiN and Cr-TiN thin film (a) M1, (b) M7, (c) M8, (d) M9, (e) M10.

4.2.2 Surface Morphology

Surface morphology of the grown films is studied by Atomic force microscopy. Two and three-dimensional $2 \times 2 \mu m^2$ AFM image of the films grown on Si substrates with the varying ratio of Cr-doping were shown in Figure 33-37 and the concerning Cr-TiN film parameters were seen in Table.8. The surface of all the films appear to have grain like structure and not much change in the morphology is observed as a function of chromium concentration. However, the root mean square surface roughness increases with the

increase in chromium concentration in the film. The average grain size slightly increases with increasing chromium in TiN film as estimated from the AFM images using Gwyddion software[76]. For sample M1 the root mean square (RMS) roughness is found to be 0.40 nm with grain size around 6.1 nm those values increase for sample M7 to be around 0.85 nm and 9.6 nm for RMS roughness and an average grain size, respectively. Where the RMS reached to 1.18 nm and the average grain size reached to 10.4 nm for samples M8, the value of the RMS roughness increases to 1.21 nm where the average grain size is decreased to 9.9 nm, for the sample M9. For sample M10 which has a high value of DC power of chromium, the RMS roughness is found to be 1.06 nm with the average grain size 6.6 nm. The results of the AFM illustrate that doping has an effect on morphology as predicted, rising the amount of DC power for cobalt, it indicated that the root mean square (RMS) roughness is increased, the lowest roughness was found at the Zero DC power for cobalt.

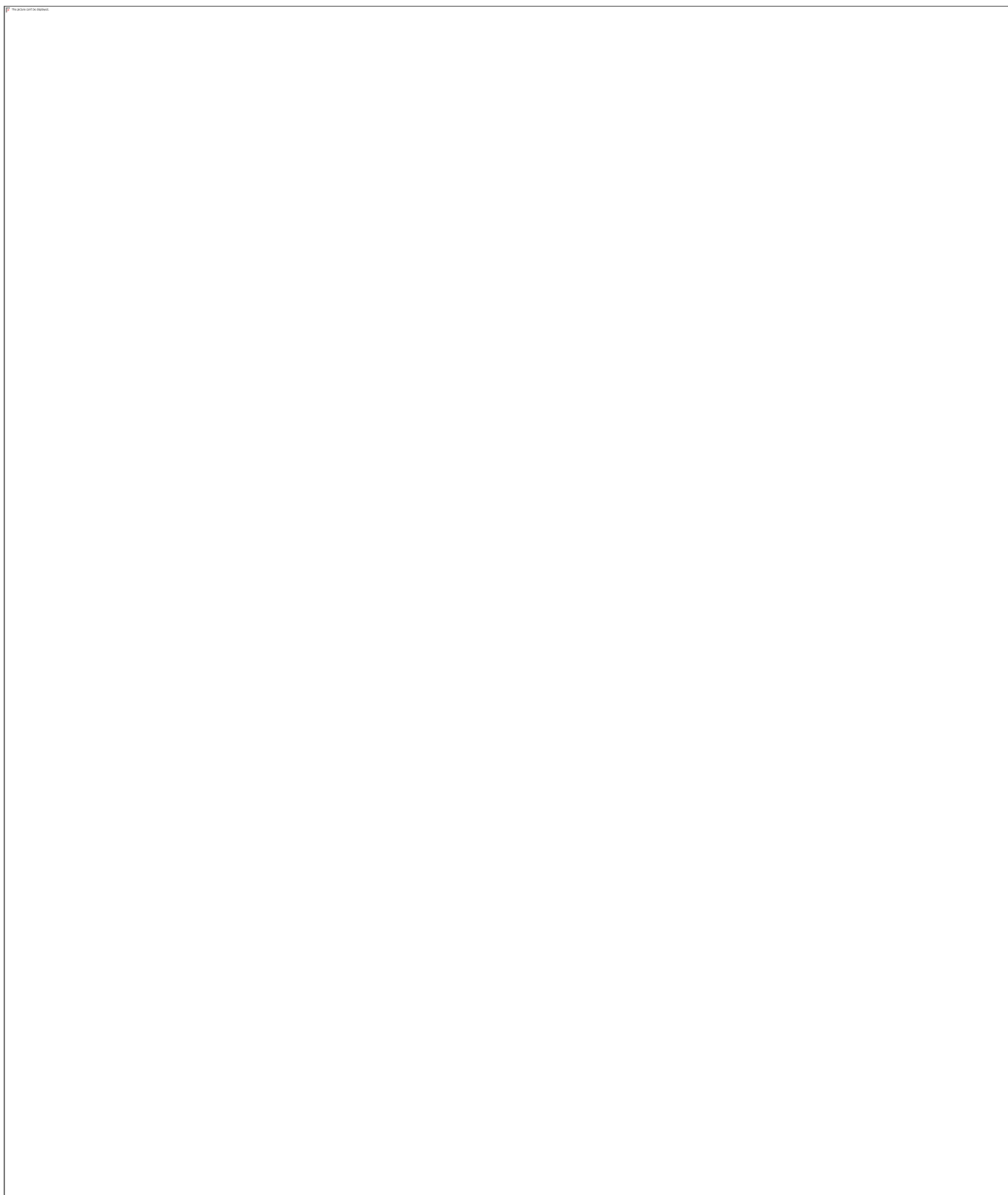


Figure 33 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M1.(a) Two- dimensional, (b) three-dimensional.

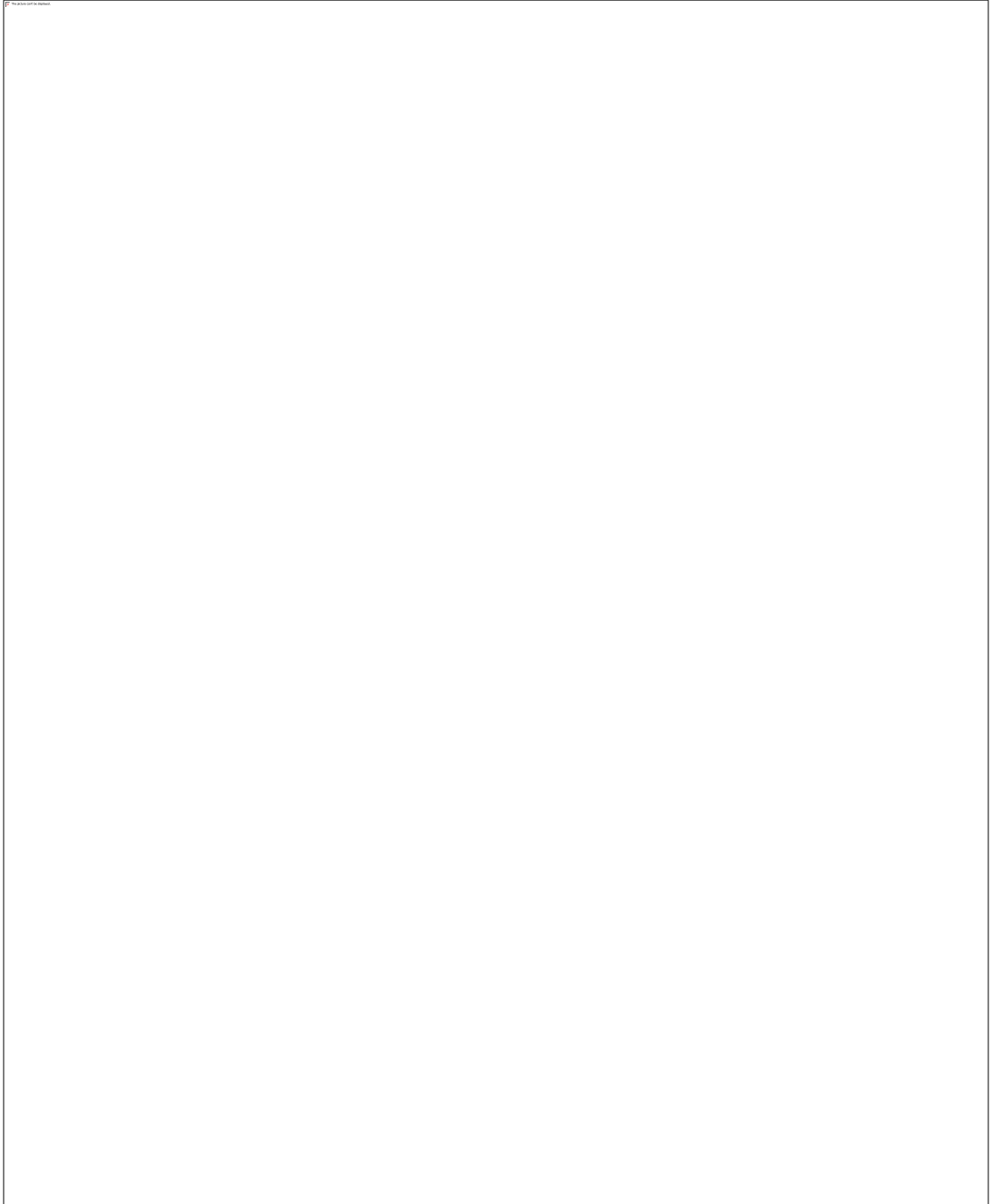


Figure 34 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M7.(a) Two- dimensional, (b) three-dimensional.

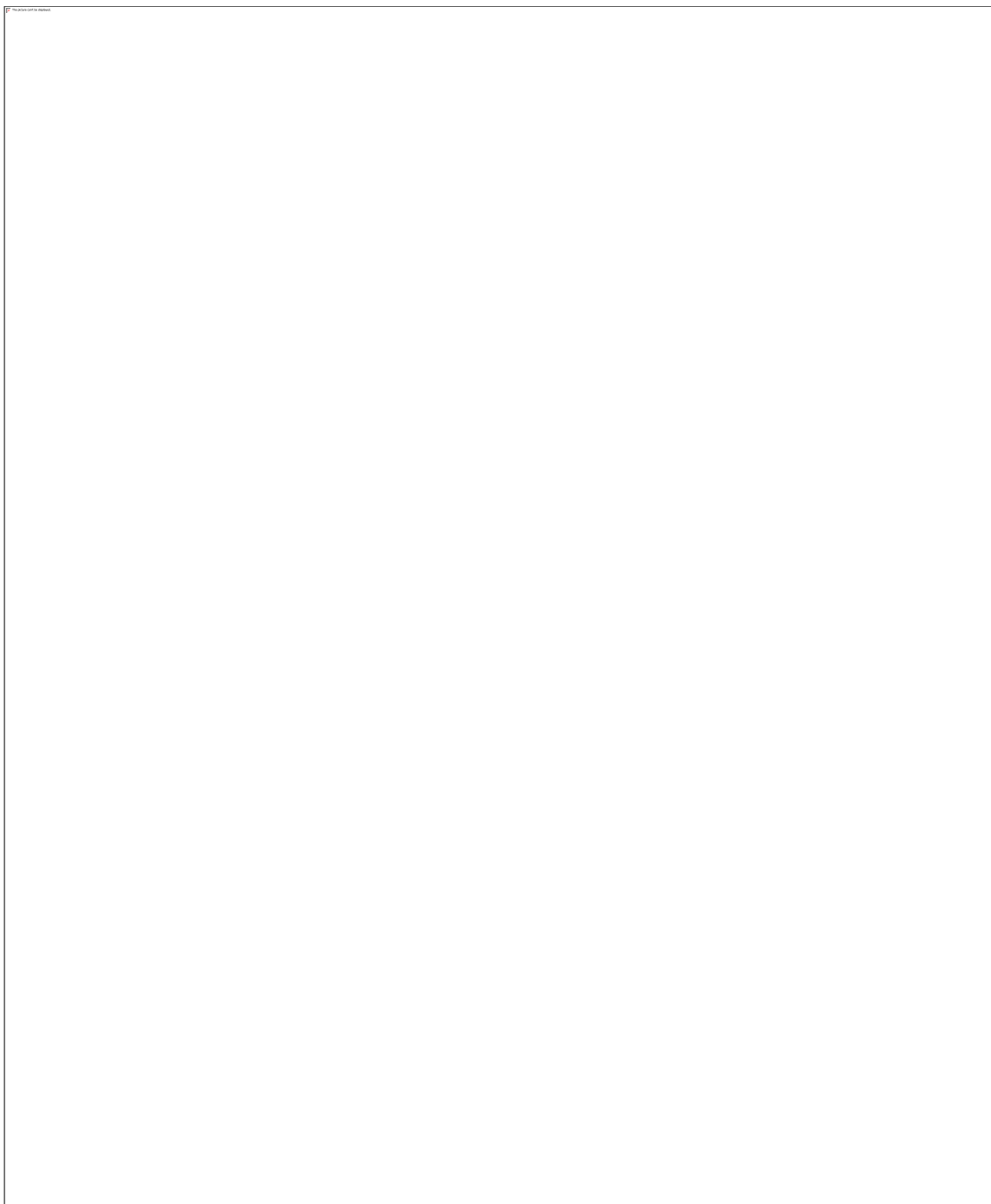


Figure 35 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M8.(a) Two- dimensional, (b) three-dimensional.

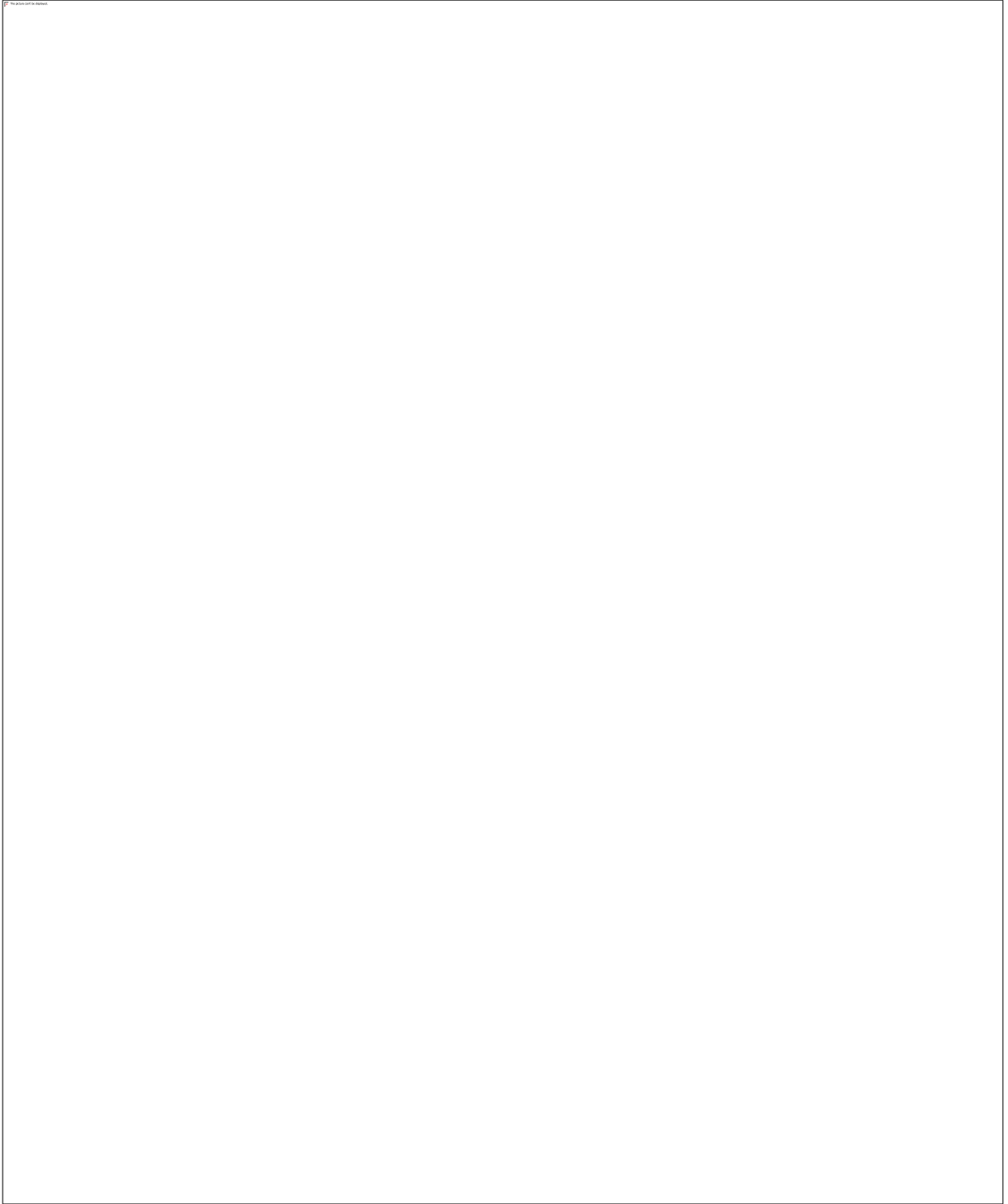


Figure 36 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M9.(a) Two- dimensional, (b) three-dimensional.

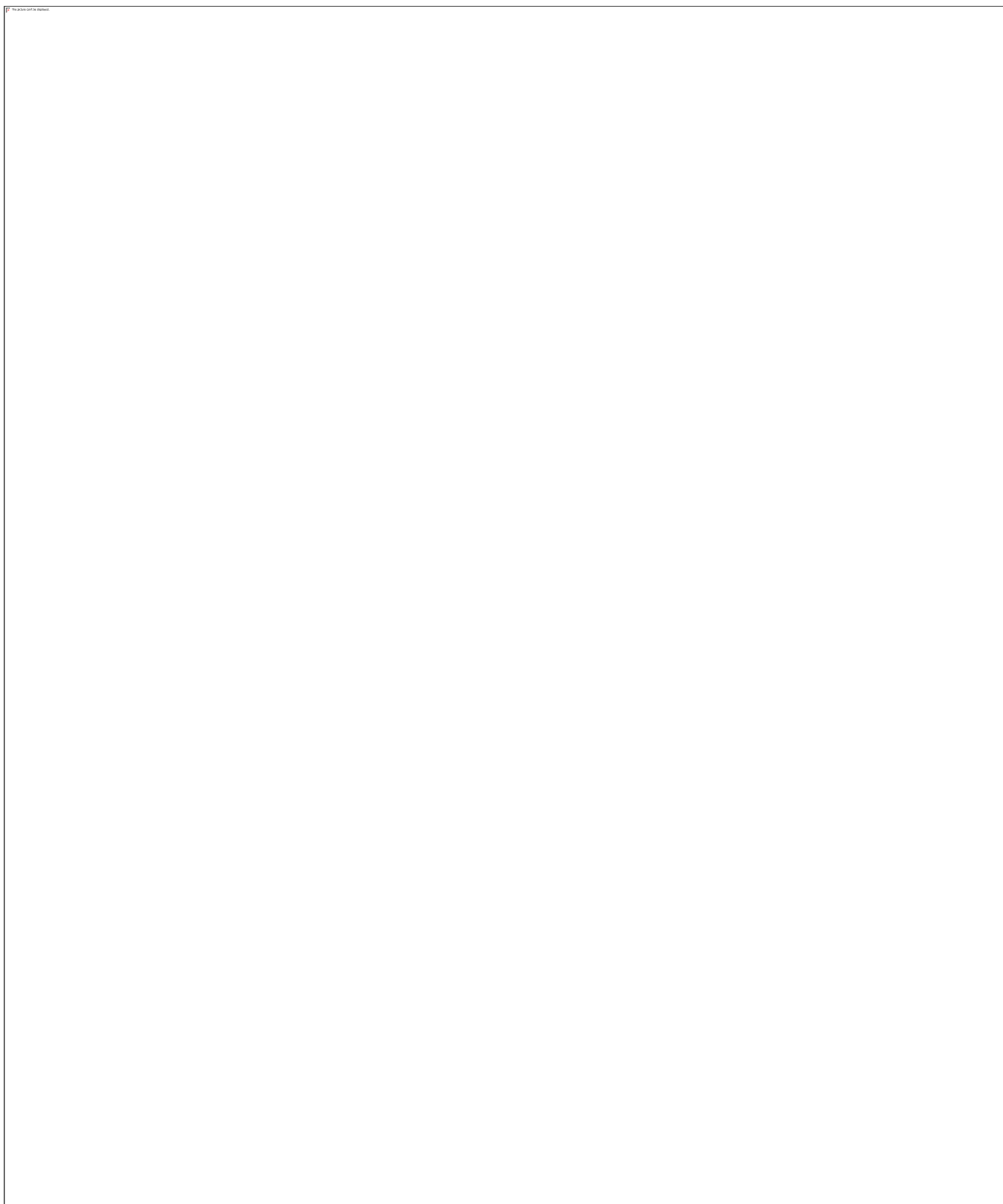


Figure 37 AFM images with size $2 \times 2 \mu\text{m}^2$ of sample M10.(a) Two- dimensional, (b) three-dimensional.

Table 8 Average surface RMS roughness and average grain size measured by AFM.

Sample#	Average Surface RMS roughness (nm)	Average Grain size estimated by AFM (nm)
E31-M1	0.4 ± 0.04	6.1
E38-M7	0.85 ± 0.16	9.6
E39-M8	1.18 ± 0.21	10.4
E40-M9	1.21 ± 0.13	9.9
E42-M10	2.44 ± 0.30	6.6

4.2.3 Optical study

The transmission spectra of the Cr-TiN films are shown in Figure 38. The transmittance of the films was used to calculate the band gap and thickness of the films using the following relation[58, 69]:

$$d = \frac{\lambda_{max} \times \lambda_{min}}{4n_f |\lambda_{max} - \lambda_{min}|}$$

where λ_{max} and λ_{min} are the wavelengths of adjacent maximum and minimum in the transmittance spectrum, respectively. Where d is the film thickness and n_f is the refractive index of the film. The refractive index can be calculated by determine the minimum transmission (T_{min}) and using the empirical relation[58, 69]:

$$n_f = 4.22 - 2.94T_{min}$$



Figure 38 Transmittance spectra of the films grown at different DC power of Chromium.

In order to be confident of the thickness of the films, we performed a thickness measurement again using SEM. The thickness of the Cr-TiN films was measured using the top-view and cross-section SEM images in Figure 39. The films' thickness is found to be between (96 nm to 118 nm). We calculated the bandgap of the films by taking the average of all these thickness measurements.

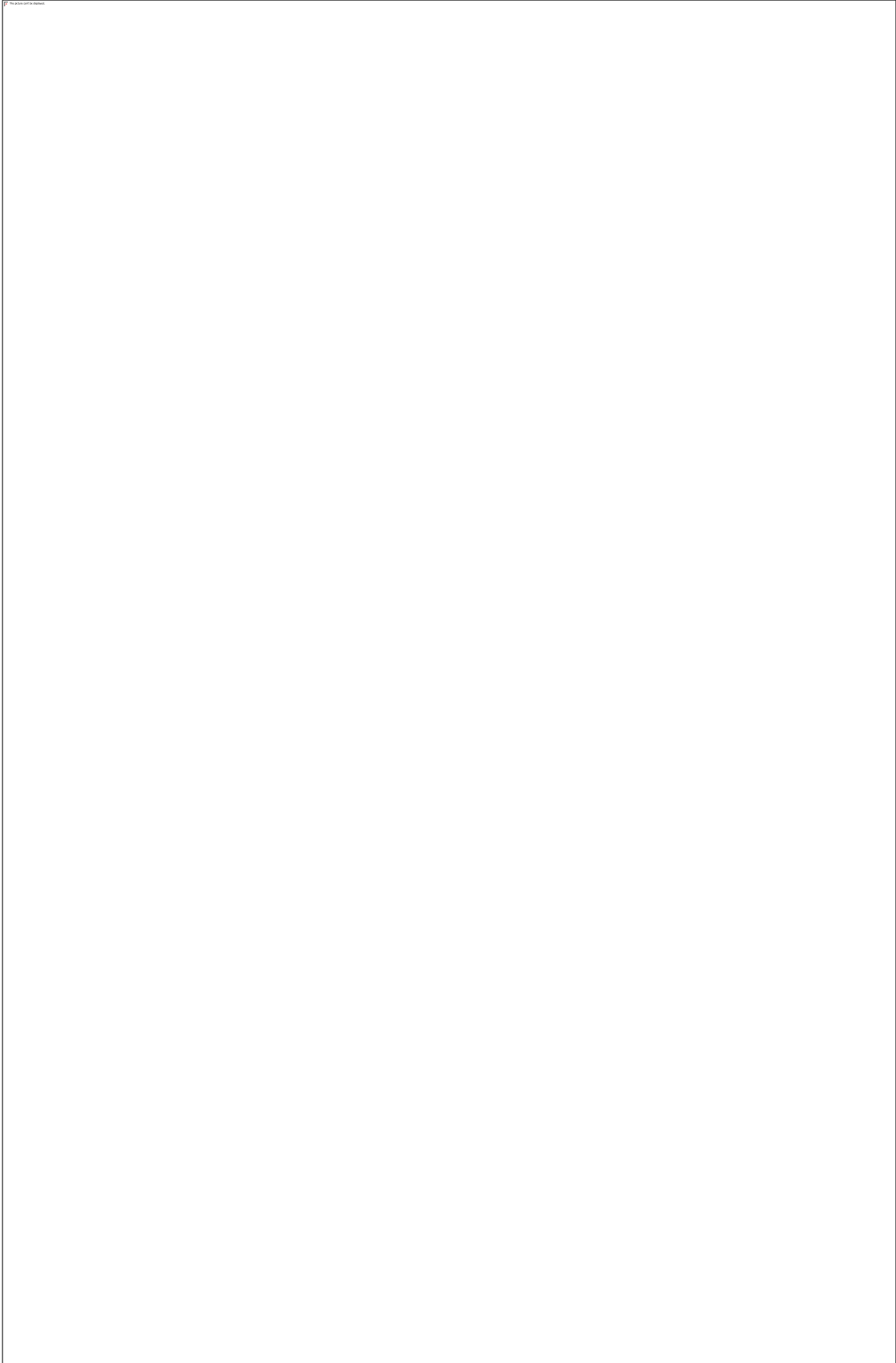


Figure 39 Cross-section images of Cr-TiN films deposited at different DC power for cobalt using SEM. (a)M1, (b)M7, (c)M8, (d)M9, (e)M10.

The band gap of the films can be determined using the following relation for a direct bandgap material [56, 58, 69].

$$(\alpha E)^2 = \beta(E - E_g)$$

Where β is a constant, α is the absorption coefficient, E is the energy of the incident photon and E_g is the bandgap of the material. By plotting $(\alpha E)^2$ as a function of incident photon energy (called TAUC plot), the bandgap of the film can be determined by extrapolating the linear portion of the curve to the x-axis.



Figure 40 Tauc plot of the films grown at different DC power of Chromium.

Shown in Figure 40 are the TAUC plots of Cr-TiN films, the bandgap of the film decreases with the increase in chromium concentration in the film. The bandgap values as determined from the TAUC plots are given in Table 9. The decrease in bandgap of Cr- TiN films as a

function of chromium concentration could be due to formation of gap states by chromium dopants.

Table 9 Thickness and band gap of Cr-TiN films.



4.2.4 XPS study

XPS analysis of Cr-TiN films were performed to study the existence of various elements in the films, their relative concentration and oxidation states. Surface of the films were etched by low-energy Ar ions for 30 s to remove any organic contaminants from the surface of the film that are deposited after the growth when films are exposed to air before transferring them to the XPS chamber. Carbon peak C1s at binding energy 284.8 eV was used to correct the XPS spectrum due to any charging effect. The high-resolution XPS corrected spectra of Ti2p_{3/2}, N1s, O1s and Cr2p_{3/2} in the films taken after 30 s etching of the film are taken out.

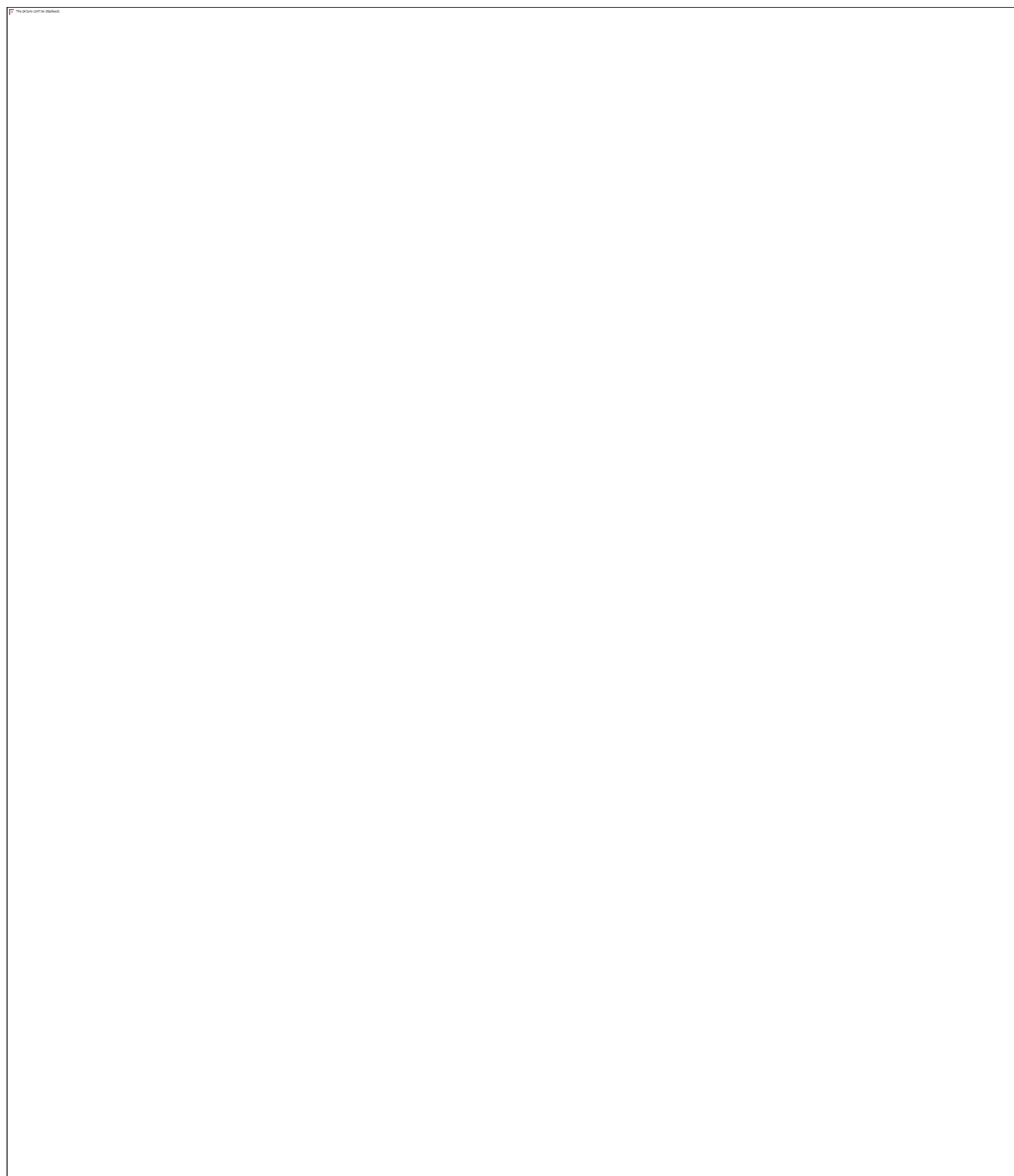


Figure 41 High resolution XPS spectra of (a) $\text{Ti}2p_{3/2}$ for sample M10 with its deconvoluted peaks, (b) $\text{Ti}2p_{3/2}$ for all the samples.

Due to spin-orbit coupling, $\text{Ti}2p$ and $\text{Cr}2p$ XPS spectra are split into two peaks $\text{Ti}2p_{3/2}$, $\text{Ti}2p_{1/2}$ and $\text{Cr}2p_{3/2}$, $\text{Cr}2p_{1/2}$ respectively but shown here only $\text{Ti}2p_{3/2}$ and $\text{Cr}2p_{3/2}$. Figure 41(a) shows a high-resolution XPS spectrum of $\text{Ti}2p_{3/2}$ for sample E42 with the peak fitting analysis using Advantage software. $\text{Ti}2p_{3/2}$ spectrum consists of three peaks with binding energies 455.8 eV, 457.1 eV and 458.7 eV that correspond to TiN, titanium oxynitride

(TiN_xO_y) and TiO_2 [58, 77, 78]. Exact peak positions of all the samples are given in table.10.



Figure 42 High resolution XPS $\text{Ti}2p_{3/2}$ spectra for the grown thin films with their deconvoluted peaks. (a) M1, (b) M7, (c) M8, (d) M9.

Shown in Figure 41(b) are $\text{Ti}2p_{3/2}$ spectra for all the grown films samples overlaid on top of each other. It can be observed that for samples with no chromium doping (M1), the intensity of TiN peak is lower compared to the intensity of TiO_2 related XPS peak. Although oxygen was not intentionally doped in the film but was chemisorbed after the growth when samples were taken out of the chamber and exposed to air. Chromium doping in titanium nitride results in increase of the intensity of TiN peak compared to the intensity of TiO_2 peak. For sample M10 with the highest chromium concentration the intensity of TiN peak becomes higher than the intensity of TiO_2 peak. This indicates that chromium increases the solubility of nitrogen in the film and similar effect of increased nitridation of

TiN was observed in cobalt doped TiN and iron doped TiN [58]. Ti2p_{3/2} spectra of sample M1, M7-10 are deconvoluted and shown in Figure 42 and the peak position of deconvoluted peaks are given in table.10.

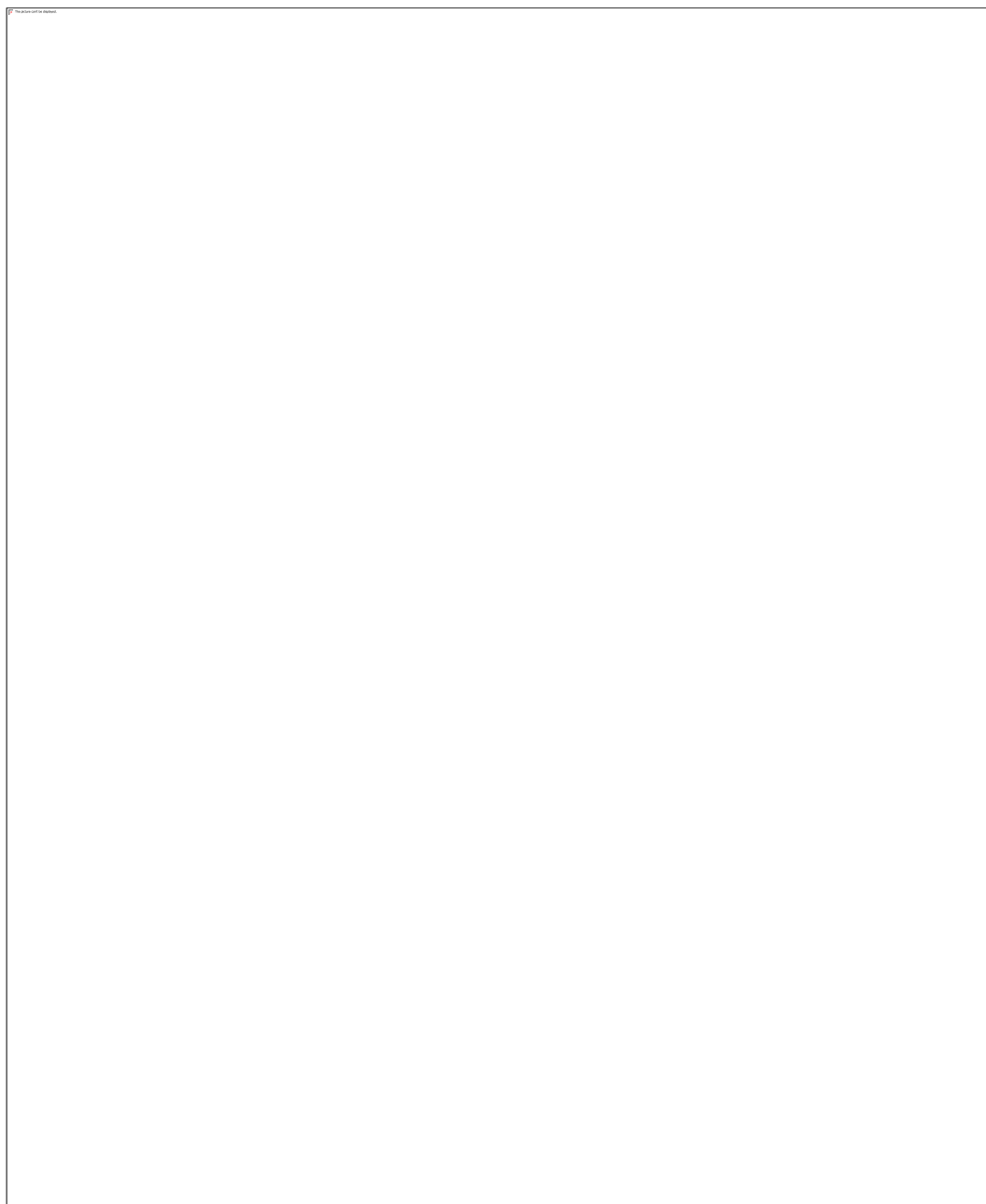


Figure 43 High resolution XPS spectra of (a) N1s for sample M10 with its deconvoluted peaks, (b) N1s for all the samples.

Shown in Figure 43(a) is N1s XPS spectra of sample M10. Using the peak fitting analysis N1s spectra was deconvoluted into two peaks, the first peak centered around 397.4 eV is due to Ti-N bond and the second peak centered around 398.5 eV corresponds to TiN_xO_y [57, 79]. Shown in Figure 43(b) are N1s spectra for all the grown films overlaid on top of each other. It can be observed that nitrogen peak intensity in general increases for films that were grown at higher sputtering power for chromium. Also, the ratio of TiN peak intensity to TiN_xO_y peak intensity grows with the increase in chromium concentration in the film. This observation matches very well with the Ti2p data where Ti-N peak intensity increases compared to TiN_xO_y and TiO_2 peaks with the increase in chromium concentration. Peak fitting was performed for all samples and shown in Figure 44. N1s spectra for all sample has peaks from Ti-N bond and TiN_xO_y the peak position for all samples is listed in table.10.

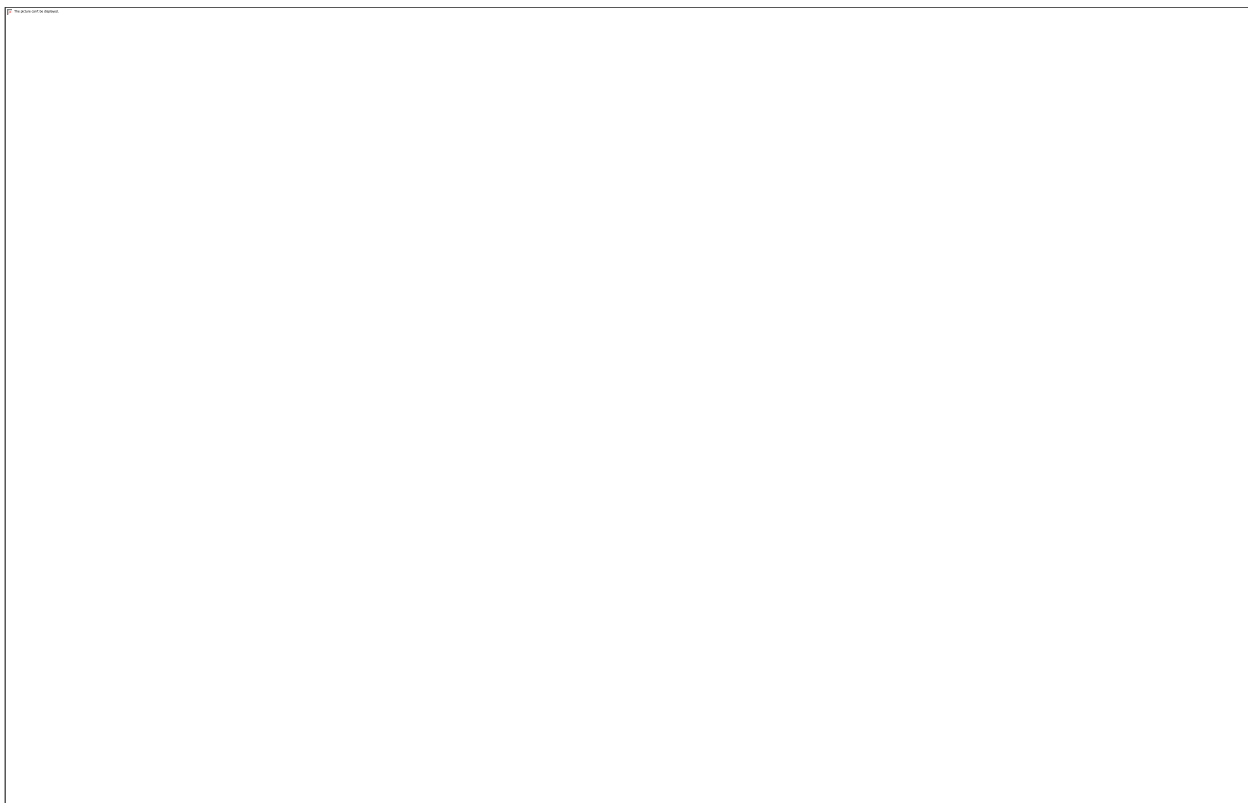


Figure 44 High resolution XPS N1s spectra for the grown thin films with their deconvoluted peaks. (a) M1, (b) M7, (c) M8, (d) M9.

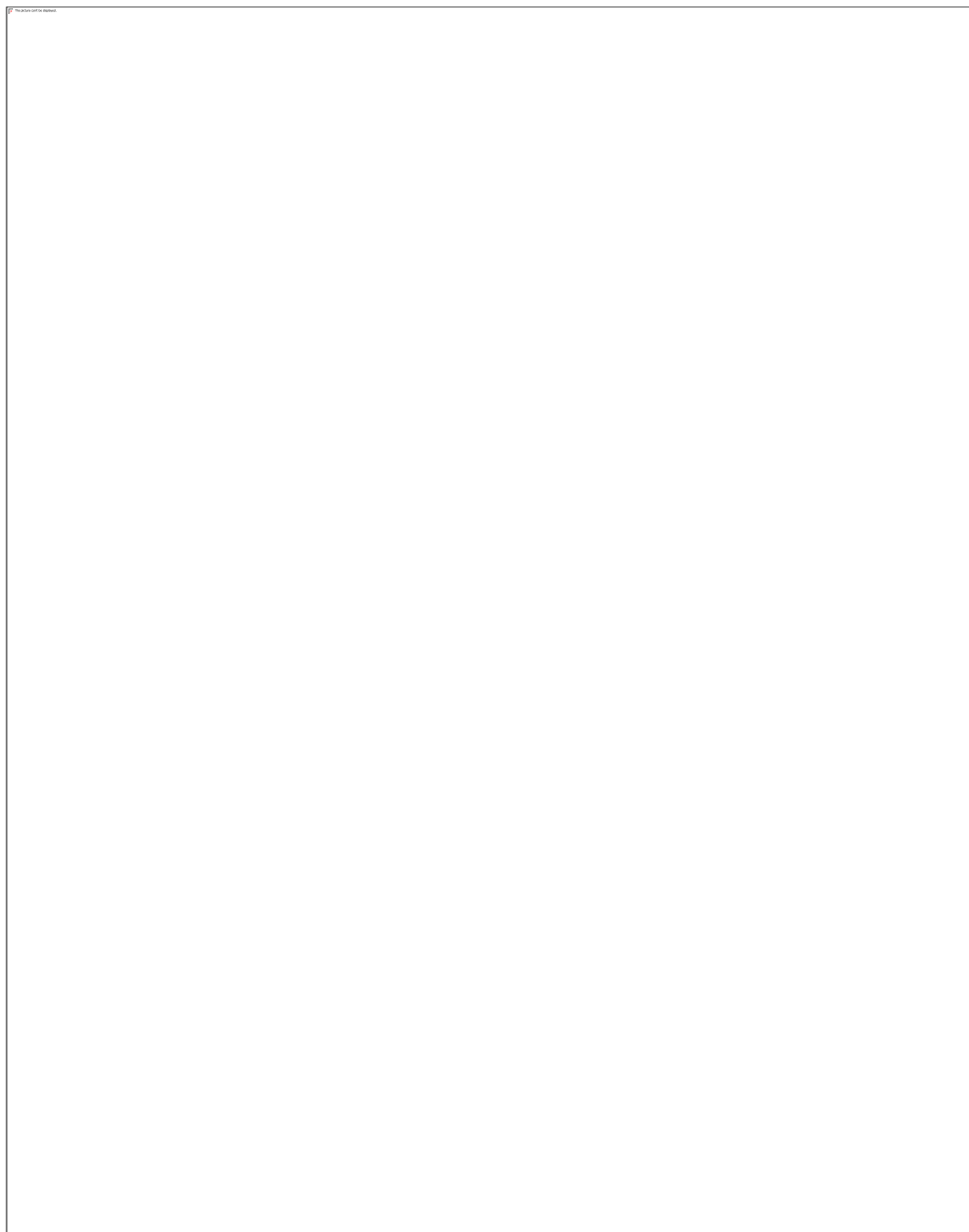


Figure 45 High resolution XPS spectra of (a) O1s for sample M10 with its deconvoluted peaks, (b) O1s for all the samples.

Shown in Figure 45(a) are the XPS spectra of O1s for sample M10 with their deconvoluted peaks. O1s spectra can be deconvoluted into two peaks centered on 531.4 eV and 532.6eV corresponding to TiN_xO_y and O-H, latter is due to moisture deposited in the film when the samples were exposed to air [85]. O1s spectra for all the grown films overlaid on top of

each other were shown in Figure 45(b) It can be observed that from the Figure 46 and Figure 46 samples with higher chromium concentration like M8, M9 and M10, the center of the O1s peak shifts towards the O-H peak side compared to the peaks of samples with lower or no chromium concentration. This observation is in accordance with N1s and Ti2p spectra that chromium doping results in enhanced nitridation (Ti-N bond) of the film and hence lower Ti-O bonding. For all other samples, the comprised peaks for O1s spectra are demonstrated in Figure 46 and the binding energy is summarized in table.10.



Figure 46 High resolution XPS O1s spectra for the grown thin films with their deconvoluted peaks. (a) M1, (b) M7, (c) M8, (d) M9.

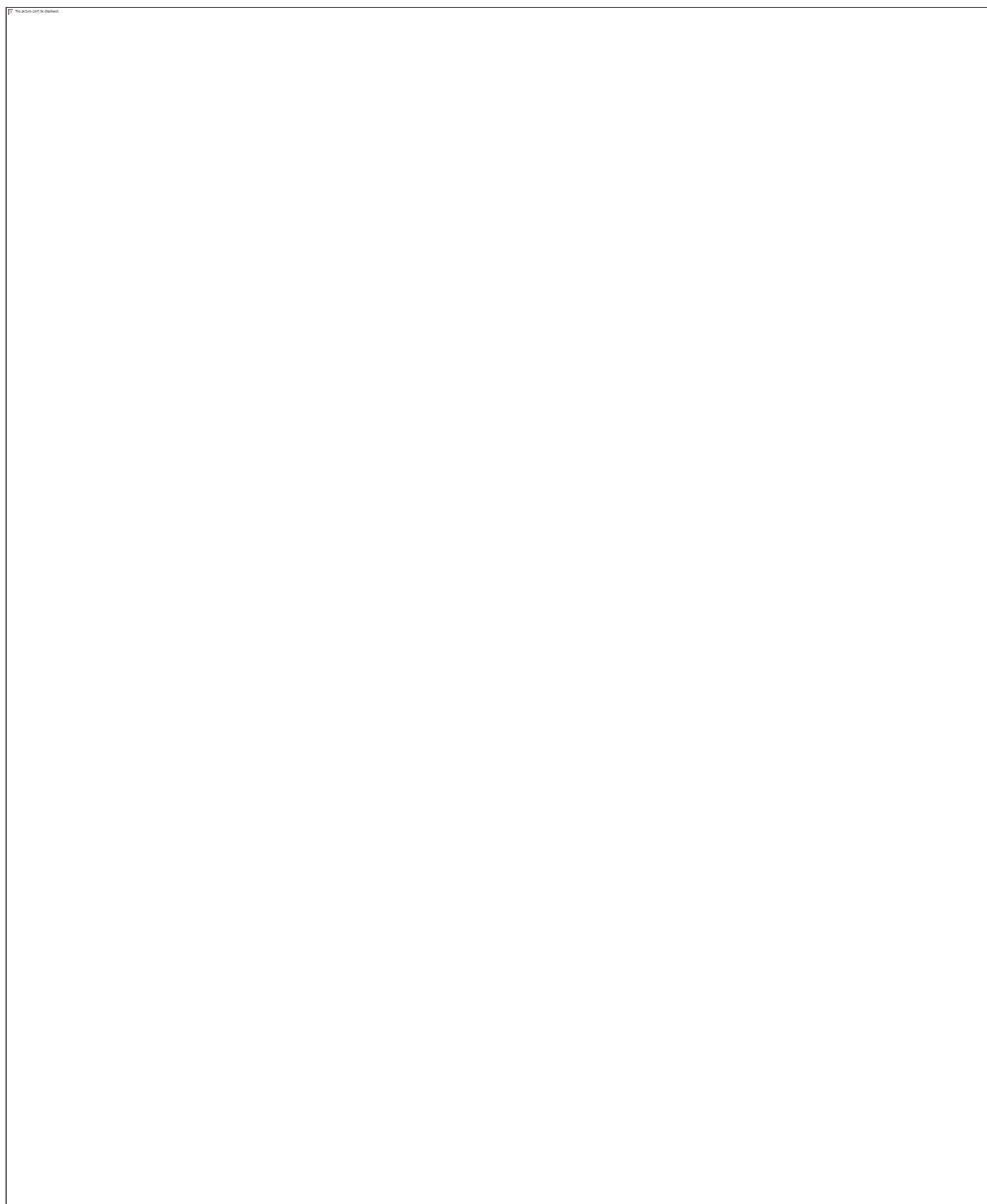


Figure 47 High resolution XPS spectra of (a) Cr2p_{3/2} for sample M10 with its deconvoluted peaks, (b) Co2p_{3/2} for all the samples.

Cr2p_{3/2} spectrum for sample M10 is shown in Figure 47(a) and Cr2p_{3/2} spectra of all the samples overlaid on top of each other is shown in Figure 47(b). The spectrum can be deconvoluted into three peaks centered at 575.6 eV, 577.9 eV and 579.9 eV corresponding to CrN, Cr₂O₃ and CrO₃ [91-93]. This shows that chromium in our samples is in third (Cr⁺³) and sixth (Cr⁺⁶) oxidation state. We can observe that, for samples with lower chromium

concentration the intensity of CrN peak is slightly less compared to Cr-O peaks, whereas for sample M10 with the highest chromium concentration the intensity of CrN peak becomes higher compared to Cr-O peaks. This indicates that samples with higher chromium concentration are mostly in the third oxidation state (Cr^{+3}) compared to the samples with lower chromium concentration. The deconvoluted for the spectra is done for other samples and shown in Figure 48 and the binding energy for all samples are summarized in table.10.

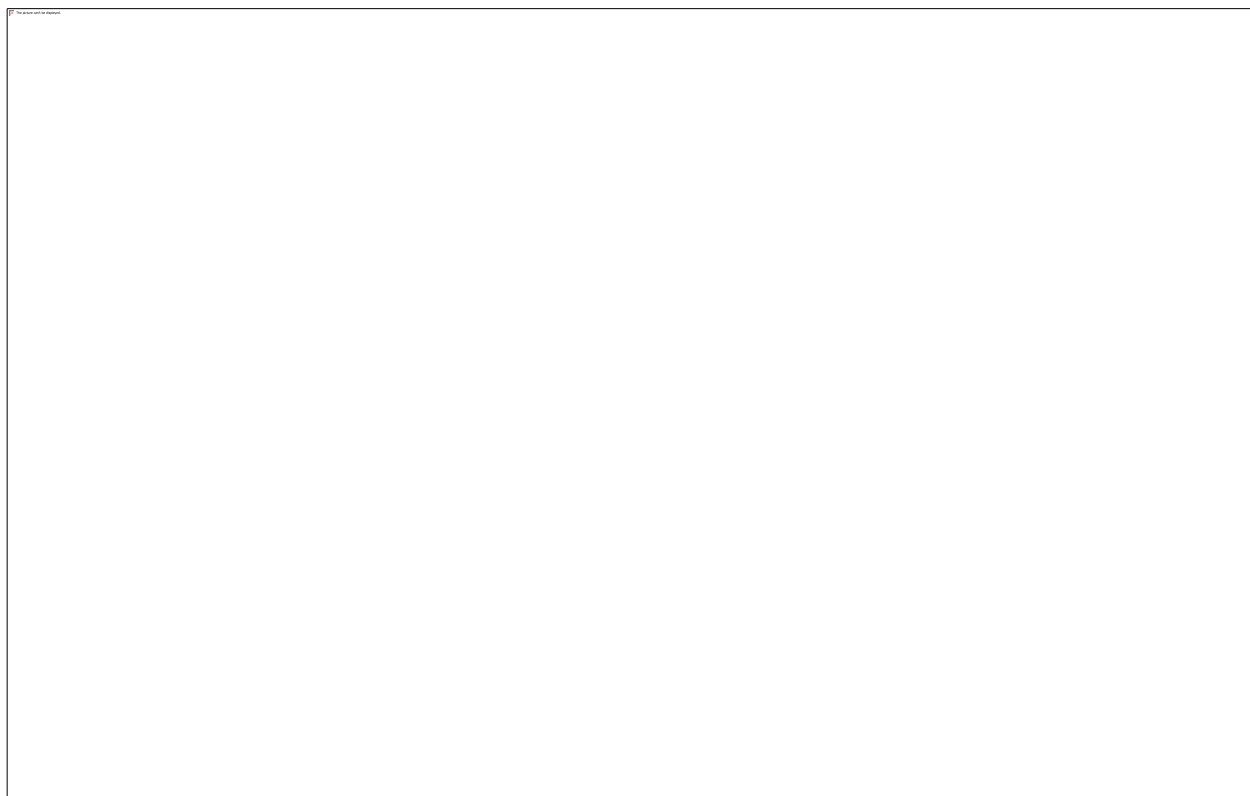


Figure 48 High resolution XPS Cr_{2p3/2} spectra for the grown thin films with their deconvoluted peaks. (a) M7, (b) M8, (c) M9.

Table 10 XPS peak positions of N1s, O1s, Ti2p_{3/2} and Cr2p_{3/2} for all samples (The values are given in eV).

Sample#	N1s Binding energy (eV)		Ti2p _{3/2} Binding energy (eV)			O1s Binding energy (eV)		Cr2p _{3/2} Binding energy (eV)		
	TiN	TiN _x O _y	TiN	TiN _x O _y	TiO ₂	TiN _x O _y	O-H	CrN	Cr ₂ O ₃	CrO ₃
E31-M1	397.5	398.6	456.3	457.7	459.5	531.4	532.6	-----	-----	-----
E38-M7	397.3	398.5	456.5	457.4	459.2	531.4	532.6	575.5	577.9	580.3
E39-M8	396.9	398.6	456.2	457.5	459.4	531.4	532.7	575.7	577.8	580.2
E40-M9	397.4	398.7	456	457.4	459.2	531.4	532.7	575.5	577.7	579.9
E42M10	397.4	398.7	455.8	457.1	458.7	531.3	532.6	575.6	577.9	579.9

CHAPTER 5

CONCLUSION

Two sets of materials were studied in this thesis work, cobalt doped titanium nitride and chromium doped titanium nitride. The thin films were prepared by RF/DC magnetron sputtering using two targets of material, sputtering titanium target using RF powered sputtering gun and cobalt/Cr with DC powered sputtering gun in the presence of N₂ and Ar gases. The DC power of the sputtering gun was adjusted (varying between 0 to 7 eV) to control the doping level in the film. The sputtered cobalt titanium nitride films and titanium nitride films were studied in detail, and it was discovered that these materials are easily oxidized to form homogeneous oxynitride layers. The optical, chemical, and magnetic properties of titanium nitride films are influenced by the concentration of cobalt or chromium dopants in the films, Since the amount of doping was the only variable in the film's growth process. The structural analysis show that the Co-TiN and Cr-TiN grown thin films are amorphous. The RMS surface roughness increases with the increasing concentration of the dopant elements. All doped TiN films are found to have RMS roughness higher than un-doped TiN films, and there is little effect of the doping on the grain size of the TiN films. For Co-TiN films, the RMS is found to be between (0.40 nm-1.70 nm) and the grain size between (6.10 nm-9.20 nm) where for Cr-TiN films the RMS is found to be between (0.40 nm-2.44 nm) and the grain size between (6.10 nm-10.40 nm). The bandgap of the film decreases with the increase the concentration of the dopant element in the film. The bandgap is found to decrease from (3.80 nm) to (3.68 nm) for Co-TiN films and to (3.56 nm) for Cr-TiN films. XPS analysis of the Co-TiN films shows the existence

of cobalt in two valence states (Co^{+2} and Co^{+3}) in a high and low spin state respectively. Where chromium in Cr-TiN films exists in the third (Cr^{+3}) and sixth (Cr^{+6}) oxidation state. The elements dopant in the titanium nitride results in an increase of the intensity of TiN peak compared to the intensity of TiO_2 peak. This indicates that cobalt (Chromium) enhances the nitridation of the film. The Co-TiN films have a weak magnetization that coexists with the substrate's strong diamagnetic backdrop, as seen by their magnetic measurements. The hysteresis does not show any apparent coercive field for the films with higher cobalt concentrations, and the films exhibit the characteristics of superparamagnetic or paramagnetic environments. At the lower cobalt concentrations, the magnetization is found to be temperature-independent, and when the concentrations of cobalt are high the magnetic response becomes temperature-dependent.

Future work is needed to grow better quality crystalline films that may result in better magnetic properties and hence formation of dilute magnetic semiconductors. And also investigate the effect of the nitrogen/oxygen ratio to engineer the optical and magnetic properties of titanium oxynitride films.

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- **Ebrahim Abualgassem**, Monzer Maarouf, Abdulhakim Bake, David Cortie, Khan Alam, Muhammad B. Haider. Effect of Cr on the Properties of TiN Thin Films Grown by Reactive Magnetron Sputtering. **(In progress)**.