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# Synthesis and Properties of Titanium Nitride Thin Films Prepared by Metal Organic Chemical Vapour Deposition Technique

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## Abstract

Titanium nitride thin films were prepared by MOCVD technique from Ethylenediamine based metal organic precursor as a source material and were investigated in terms of volatility and stability by employing TG/DTA in transpiration mode, which led to thermal degradation in the temperature range of 105.9°C and 540.3°C. The effect of deposition temperature on TiN thin film deposited on soda-lime glass substrates were characterized using Ultraviolet-Visible Spectroscopy, Four-point probe technique, Scanning Electron Microscopy (SEM), optical microscope and Energy Dispersive X-ray Spectroscopy (EDS). Experimental results show that TiN thin film exhibited an amorphous behavior with honeycomb-like nature of surface roughness which depends on deposition temperature. The nitrogen atomic (%) proportion in TiN thin film increased from 46 to 51, the estimated thickness range from 152.08 to 167.29 and direct optical band gap varies from 3.62 eV to 3.68 eV as deposition temperature increases. The electrical resistivity ranging from 1.58 Ωcm to 1.81Ωcm also depends on deposition temperature. The findings showed that the synthesized precursor is a promising material for deposition of quality TiN thin films. It also demonstrates that the properties of the films depend on the deposition temperature.

## Keywords

TiN, Thin Film, MOCVD, Synthesis, Optical Property

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## 1. Introduction

Metal Organic Chemical Vapour Deposition (MOCVD) of thin films involves the chemical reactions of gaseous reactants on or near the vicinity of a heated substrate surface. It can produce single layer, multilayer, composite, nanostructure and functionally graded thin films with well controlled dimension and unique structure at low processing temperatures. The versatility of MOCVD had led to its rapid growth and it has become one of the main processing methods for the deposition of thin films and coatings for a wide range of applications. This includes semiconductors for microelectronics and optoelectronics (Vittori, 1979); metallic films and refractory ceramic materials used for protective coatings (Choy, 2003) among others.

However, the low thermal stability of the metal-organic precursor was due to their hydrolysis, which changes the rate of evaporation with time, has led to difficulties in controlling the composition of both the vapor phase and films. The synthesis of high quality films requires precursors that will undergo pyrolysis easily. The use of single source precursors also simplifies the control of the process parameters of the MOCVD process for synthesizing a compound semiconductor. The thickness of the layer, coating

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stoichiometry and the growth rate can be controlled precisely by a few parameters (such as temperature, gas flow rate) of the MOCVD process.

Recently, titanium nitride has aroused intensive interests because of its simple structure and special properties such as high melting point, high hardness, high corrosion resistance, high specific strength and metallic conductivity. It behaves like most of refractory transition metal nitrides with NaCl-type structure (Valkonen, et al., 1983). Many researchers have been devoted to various aspects of titanium nitride film growth and how the properties of the materials can be improved. These are important because of its convenience in integrating it into devices.

The most widely used MOCVD precursors for depositing TiN films are titanium alky amides such as Tetrakis-dimethylamido titanium (TDMAT) $Ti[N(CH_3)_2]_4$, tetrakis-diethylamido titanium (TDEAT) $Ti[N(C_2H_5)_2]_4$ and Tetrakis-ethylmethylamido titanium (TEMAT) $Ti[N(C_2H_5)\text{-}(CH_3)]_4$ (Shin, et al., 1996). The focus of this investigation is to synthesize and characterizes Diphenylamine ($C_{12}H_{11}N$) as a single solid source precursor for depositing TiN. The deposition and characterization of TiN thin films using the prepared Diphenylamine ($C_{12}H_{11}N$) based single solid source precursor is also reported.

## 2. Materials and Method

### 2.1. Precursor Preparation and Characterization

The diphenylamine based single solid metal organic precursor was chosen for its thermal stability, sufficient volatility, less toxicity and easy handling. The single-source solid metal organic precursor was synthesized at a laboratory scale using the following procedure: Titanium tetrachloride ($TiCl_4$) was added drop wise to diphenylamine ($C_{12}H_{11}N$) in solution of carbon tetrachloride ($CCl_4$), while heating and stirring for 2-hours. The resulting precipitate was filtered, washed with ethanol and dried over anhydrous calcium chloride. The precipitate was then dissolved in a solution of dichloromethane ($CH_2Cl_2$) and distilled water to remove any trapped chloride ions. The final product was heated at a very low temperature and finally left to dry over anhydrous sodium sulfate. Figure (1) represents the precursor reaction mechanism as shown in the equation below.

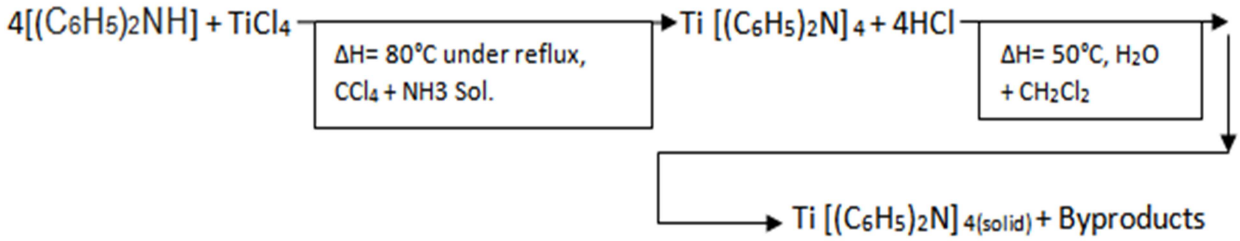



**Figure 1.** Reaction mechanism of the synthesized metal-organic precursor.

Thermogravimetric and differential thermal analyzer (TG/DTA) operating at ambient room temperature to 1100°C complimented with Gallekamp melting point analyzer was used to study the decomposition patterns and relative thermal stabilities of the diphenylamine based precursor. Scanning electron microscope (SEM) with energy dispersive x-ray (EDS) facility attached to it was also used to study the morphology and elemental composition of the precursor.

### 2.2. Thin Film Deposition and Characterization

Prior to the deposition, all the substrates were ultrasonically cleaned in heated acetone, methanol, Iso-propanol and distilled water. Figure (2) shows the thin film reaction mechanism and the schematic diagram of the MOCVD set-up (Ajayi, et al., 1994). The Diphenylamine based precursor was poured into the receptacle and nitrogen gas was blown through at the rate of 2.5 $dm^3$/min, transporting the precursor into the working chamber. The working chamber was maintained at the deposition temperature by an electrically heated furnace. The deposition was carried out at temperature of 400°C, 420°C and 450°C for 2 hour period each. In the hot zone, the precursor first sublimed before thermal decomposition, resulting in the formation of the coatings. This method does not require a pump to remove the by-products as they are swept out by the carrier gas.

Various process parameters such as substrate temperature, precursor chamber temperature (based on the temperature and the congruent sublimation temperature of precursor), carrier gas flow rate, were optimized by carrying out repeated trial and error experiments for the deposition of TiN films in order to ensure complete vaporization and transportation of precursor vapor continuity to the MOCVD chamber; evaporation of the solvent and removal of organic residuals. This helped in achieving uniform thin-film over the substrates and optimization of MOCVD technique condition reported by Ajayi (Ajayi, et al., 1994) in the nitrogen gas environment.

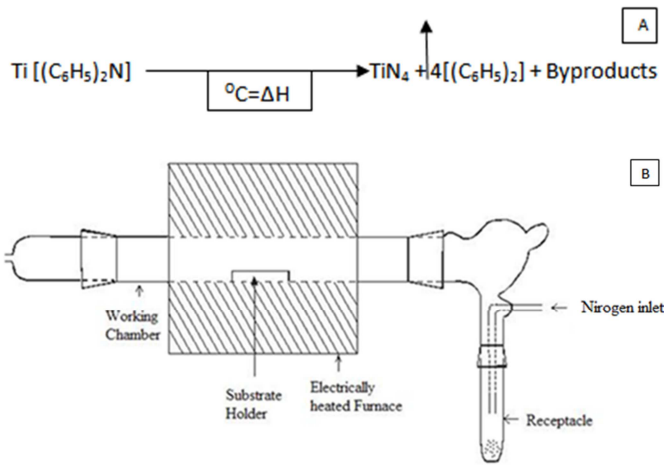


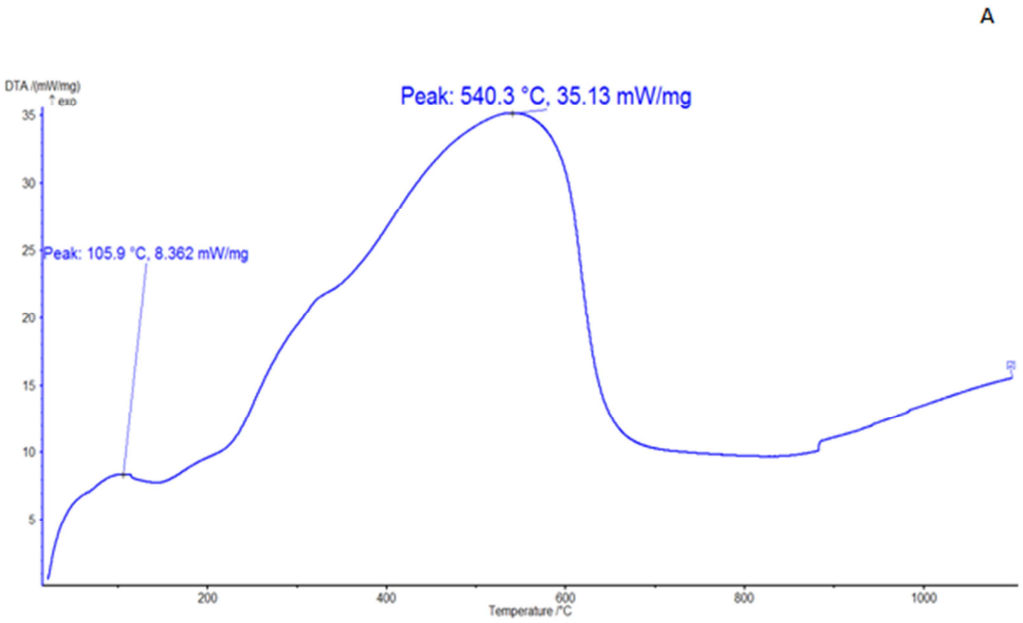

**Figure 2.** (A) TiN thin film reaction mechanism and (B) Schematic diagram of the MOCVD system used in the present study.

The surface morphology of the films was carried out with optical microscopy technique using AP2000 MTI Optical Microscope and SEM while the EDS facility attached to it was used to study the elemental composition. The optical properties analysis of the thin films was done by obtaining the absorbance spectrum using a Jenway Ultraviolet-Visible spectrophotometer (Model 6405) at normal incidence scanning wavelength between 200 nm and 1100 nm. Electrical characterization of the films was performed using four point probe method. The four point collinear probe configuration was employed. High purity silver paste baked at temperatures of 150°C for 30 minutes was used as a contact in order to have ohmic contact and eliminate contact resistance problem. Current-voltage measurement was done using Keithley 2400 Series Source meter under illumination with a source current of 0-1 mA.

# 3. Results and Discussion

## 3.1. Characterization of Precursor

The precursor was prepared in high yield according to the reaction mechanism in Figure (1) and characterized by spectroscopic and analytical technique. From Thermogravimetric and Differential Thermal Analysis (TG/DTA) spectrum in figure 3(A), it reveals an interesting behavior regarding their oxidative cleavage patterns and relative thermal stabilities. The broad endothermic peaks were observed at 105.9°C and 540.3°C with weight loss of 8.362mW/mg and 35.13mW/mg, respectively as a function of temperature and change in physical properties. The precursor is fairly stable and completely an anhydrous as no TG (weight) loss occurred up to 105.9°C. Thermal degradation took place in the temperature range of 105.9°C and 540.3°C giving off organic ligand and the liberation of $Cl_2$ with an exothermic peak at 230.3°C which signified phase transition point. The first broad endothermic peak of 105.9°C represents the beginning of melting, vaporization and decomposition of oxide bond. The broad peak might also be due to strong nitrogen ($N_2$) bond dissociation (Hohne, et al., 2003). At temperature above 540.3°C, metal organic compound experience no further organic decomposition due to poor cleavage throughout the remaining thermal period. The temperature range used for film deposition is based on the TG/DTA analysis, which, throws light on decomposition patterns and more importantly volatility which is a primary condition for chemical vapor deposition. The EDS spectrum of the prepared precursor is shown in Fig. 3B (i). The spectrum shows the signals of Ti, N, O, C, which is the expected elements of the precursor. There is also a signal from Al which may be a contaminant from of the reagents.



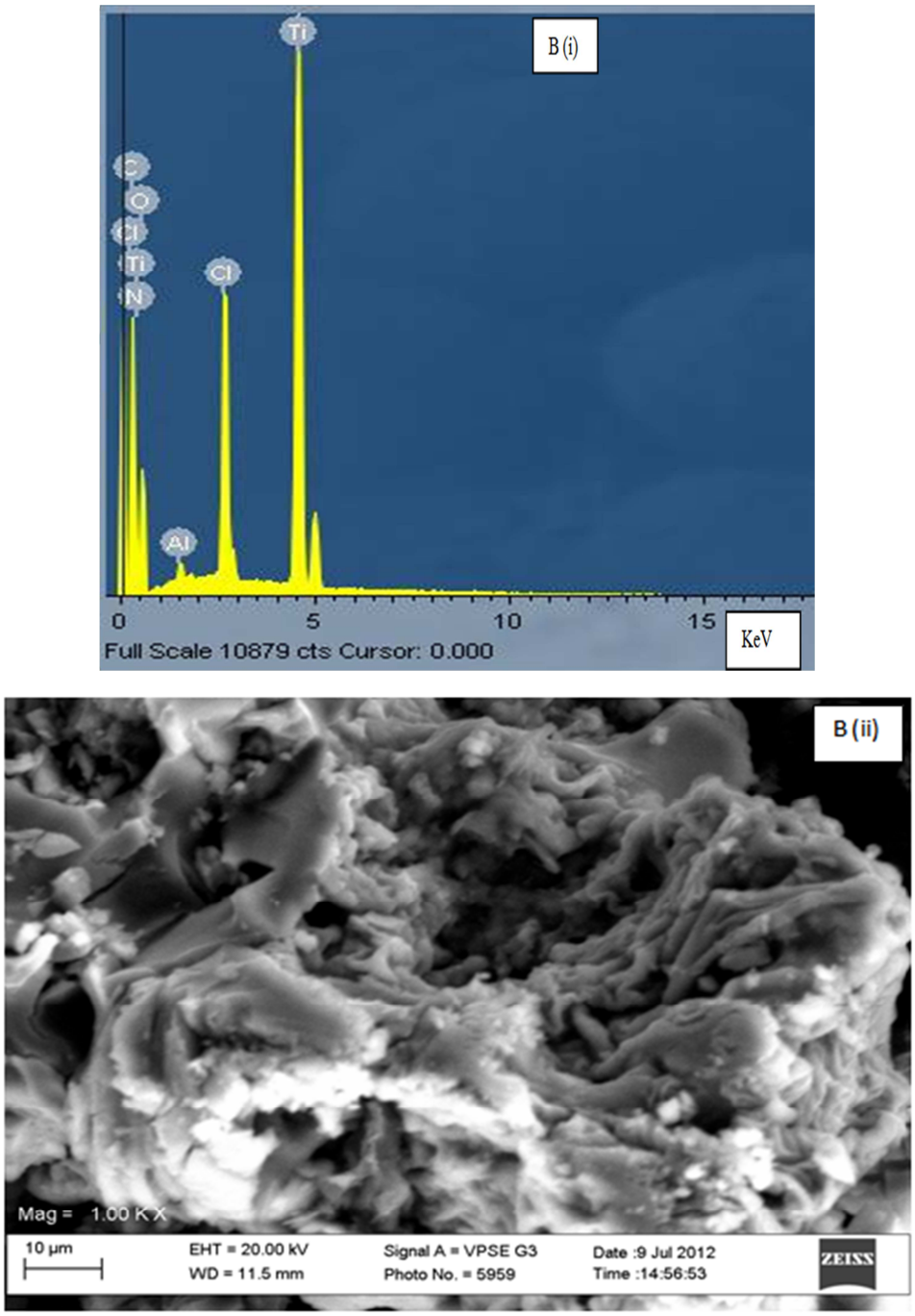



**Figure 3.** Synthesized metal-organic precursor (A) DTA heating curve, B (i) EDS Spectrum and B (ii) SEM Image.

The scanning electron microscopy (SEM) micrograph of the precursor in Figure 3B (ii) show an agglomeration of powdery solid. The reaction of Ethylenediamine with titanium tetrachloride in a salt elimination reaction for the formation of titanium ethylenediamine titanium complex is due to the thermodynamic driving force in favor of water insoluble compound formed and elimination of a large quantity of additional ligands, CO, Cl and O as by-products. It is weakly thermochromic, fairly air and moisture stable. It is insoluble in water, somewhat soluble in polar solvents like methanol, acetone and pyridine as observed.

## 3.2. Characterization of Thin Films

### 3.2.1. Surface Morphology

The surface morphology of the films was examined by SEM and complimented by an optical microscope. SEM was also used to determine the thickness of the films. Figure 4(a-c) shows SEM micrographs of the films at different deposition temperature. SEM images analysis of TiN films that were grown present highly homogenous and very compact granules with similar features at all the deposition temperature indicating that the growth mechanism is not well

defined. The small islands start coalescing with each other in an attempt to reduce the surface / areas as shown in Figure 4(a).

The thickness of the films was analyzed using the cross-sectional measurement approach on SEM images of the bare glass to deposit films. The thickness was estimated to be 152.08 nm, 159.67 nm, 167.28 nm for temperatures 400°C, 420°C and 450°C respectively. The thickness increases with increase in deposition temperature, which is in agreement with the work of Seong et al. (Seong, et al., 2006). This was attributed to the fact that the rate of deposition, increase more quickly than the rate of nucleation. Therefore, the long-reach order characteristic of crystals is not fully achieved. The increase in thickness as a function of temperature also establishes that the surface reaction kinetics that influences the rate of ordering and surface molecular mobility increases as temperature increases (Bolutife, et al., 2014).

SEM micrographs were complemented with optical micrographs which were analyzed using IMAGE-J software to obtain surface roughness (Figure 5). It can be seen that the surface roughness of the films is very sensitive to deposition temperature. The surface roughness showed a honeycomb-like structure which becomes more pronounced at 450°C. This may probably be due to the reaction rate becoming more temperature sensitive with nuclei forming faster than the product is able to diffuse across the surface to an already established growth center (Johausson, et al., 1988).

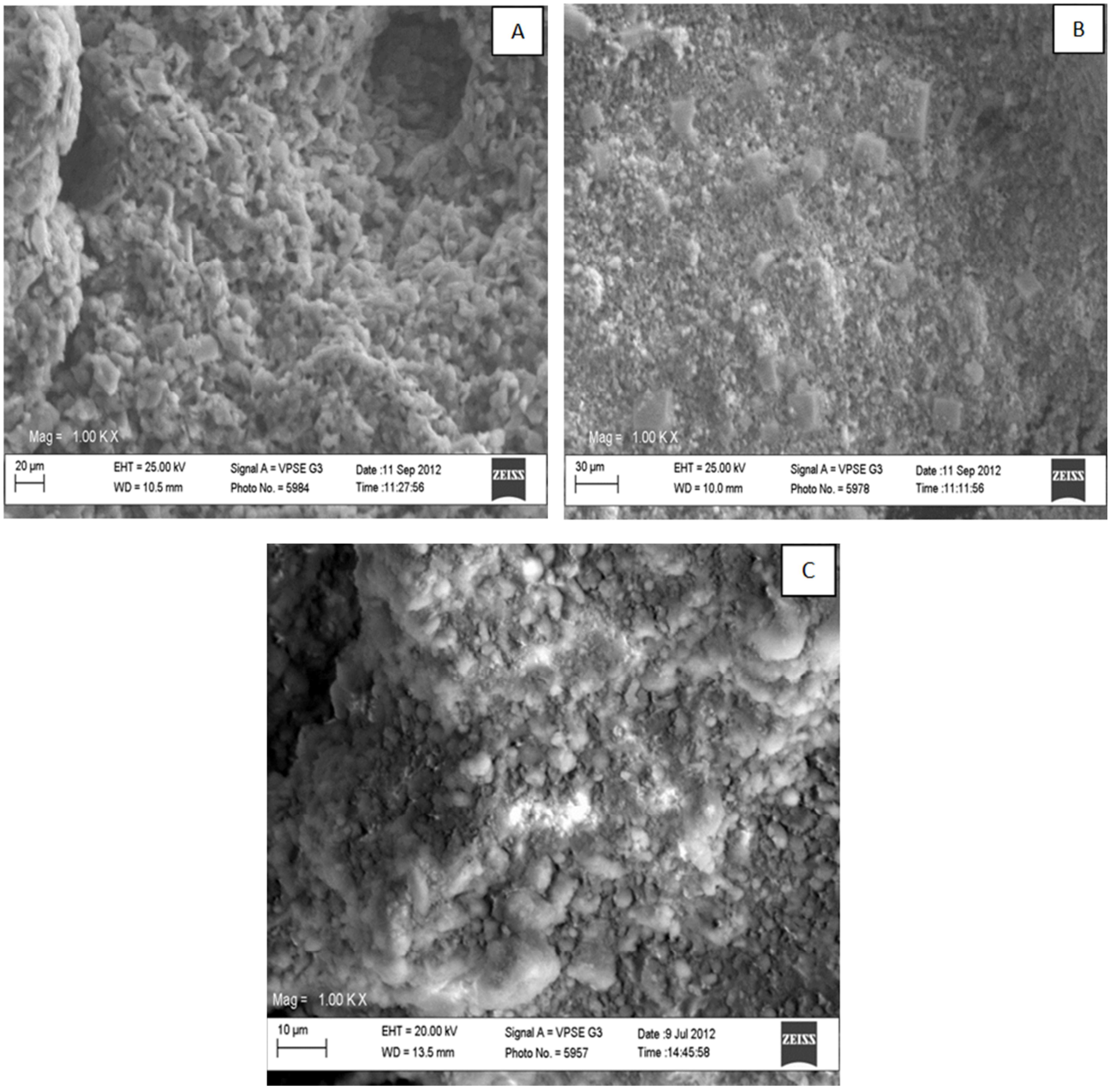
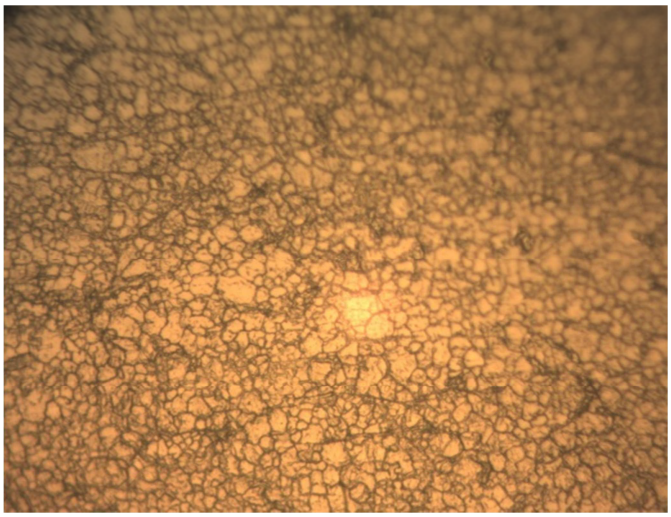
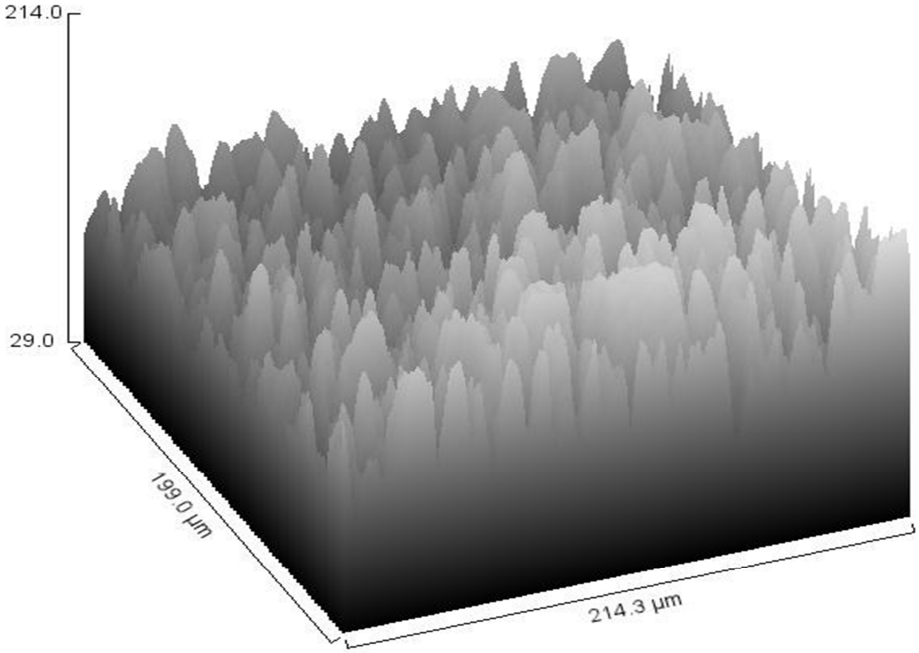


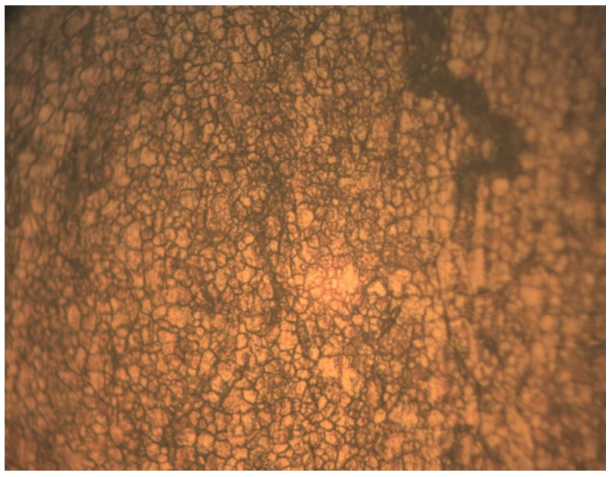

**Figure 4.** SEM Micrograph of deposited film at: (a) 400°C; (b) 420°C and (c) 450°C.



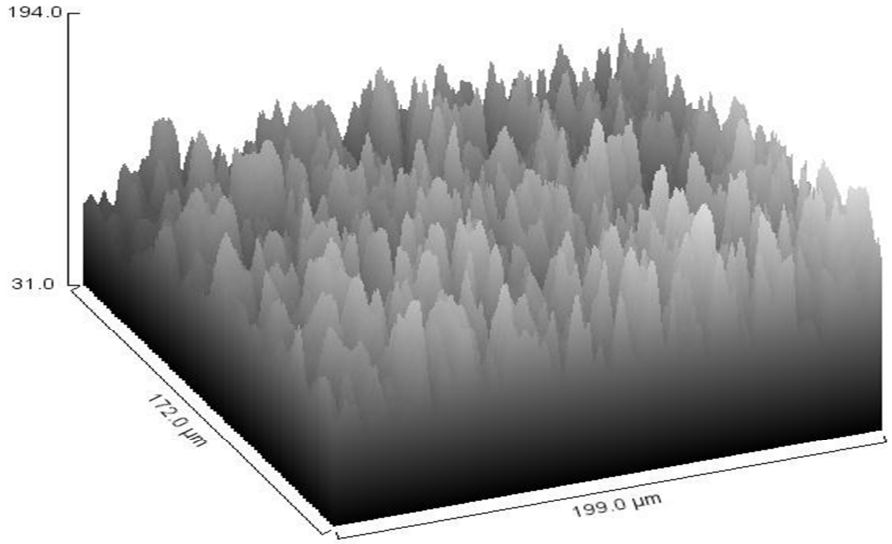
a(i)



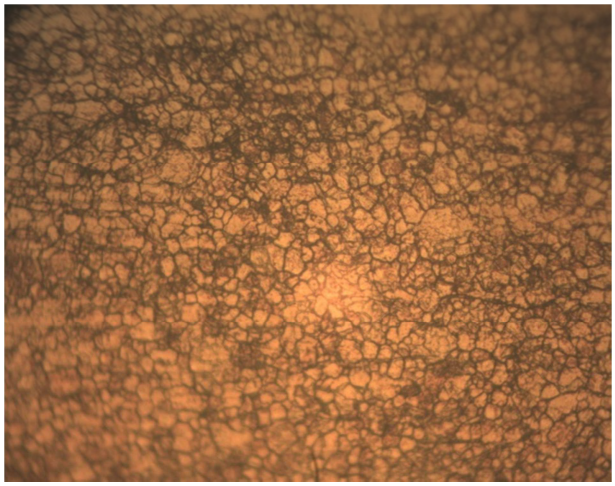

a(ii)



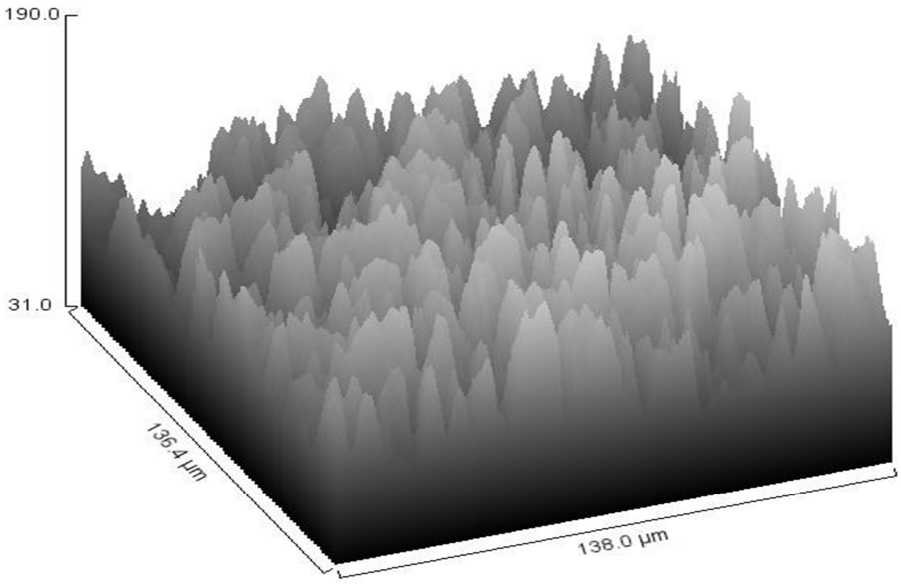
b(i)




b(ii)



c(i)

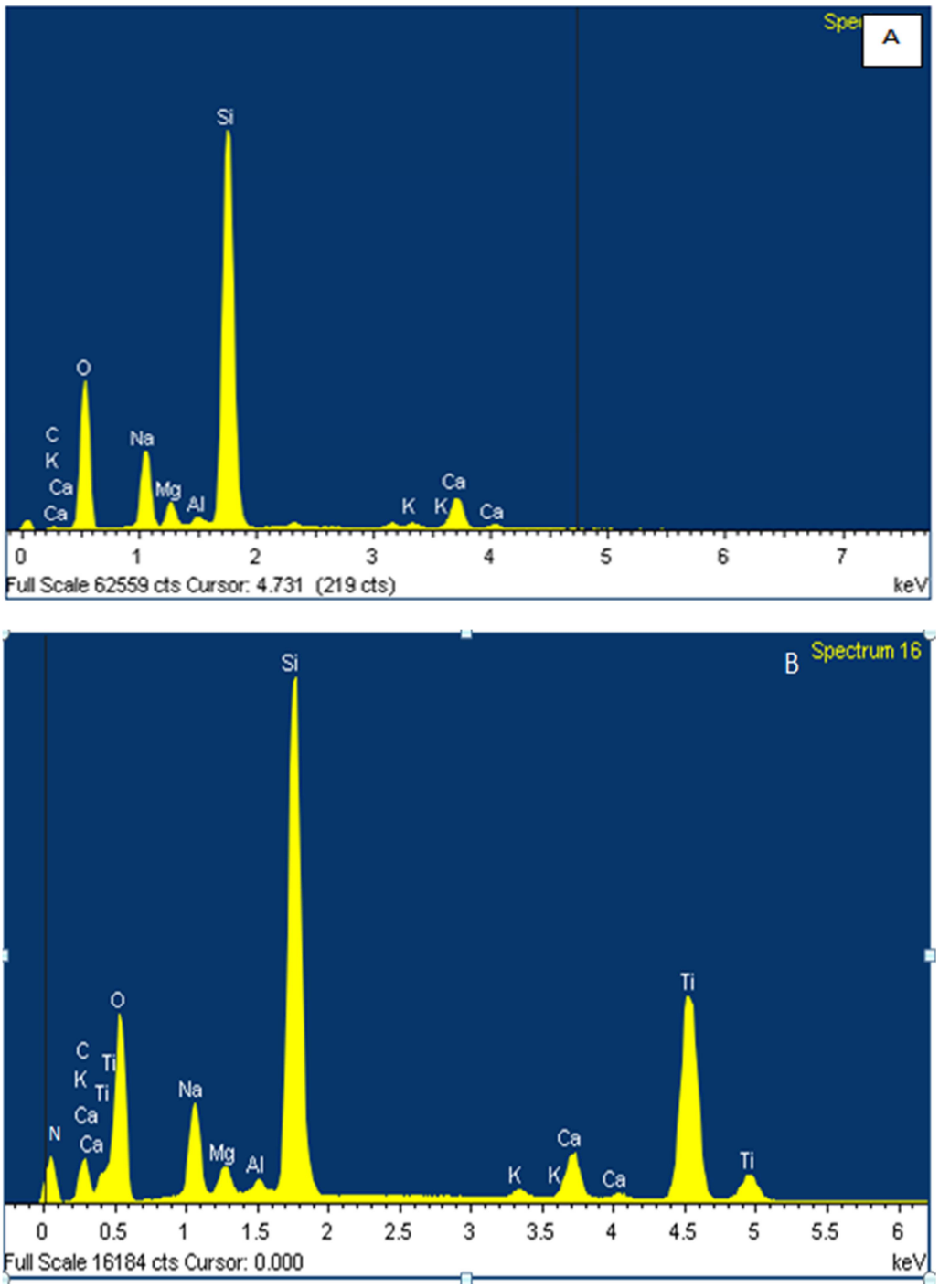



c(ii)

**Figure 5.** Optical micrograph (400X) and 3D surface roughness of films deposited on soda-lime glass at 400°C, 420°C and 450°C respectively.

### 3.2.2. Chemical Composition

The elemental composition of thin films was determined through energy dispersive X-ray analysis (EDS) from backscattered electron in the SEM. The EDS spectrum for each of the film is shown in Figure 6. Intense peak identified as the elements of the deposited films and the glass substrate (soda lime glass) used can be seen. The result shows that the relative atomic percentage of nitrogen in the film increases while varying the deposition temperature from 400°C to 450°C. The analysis reveals that the stoichiometry ratio (Ti/N ratio) was influenced by the deposition temperature. The EDS also indicates oxygen impurity that coexists with the expected Ti and N in all the deposited TiN films. This is as a result of higher reactivity of oxygen as compared to nitrogen. Therefore, the physicochemical mechanisms involved in the growth are the same for nitrogen molecules as for oxygen molecules (Martin, et al., 2001).



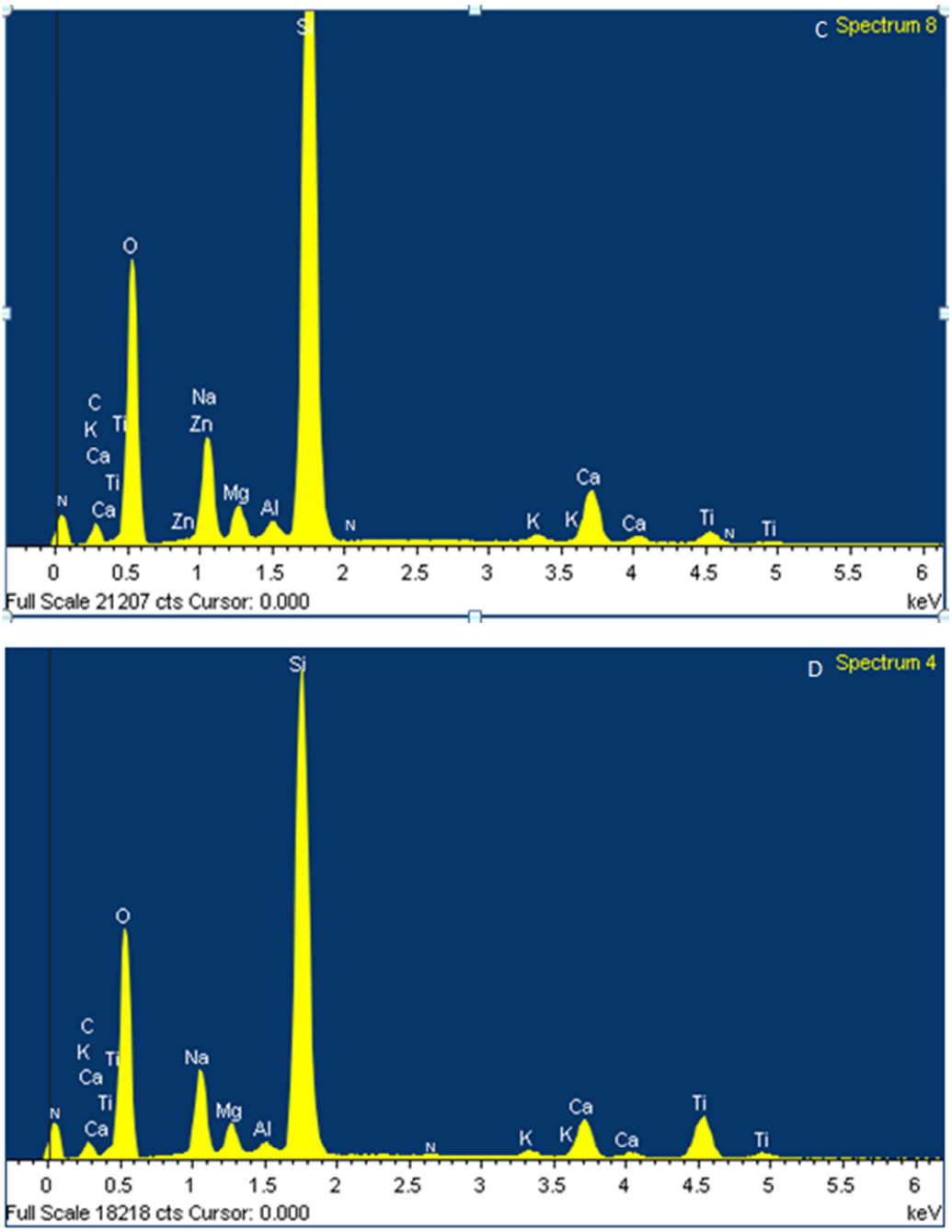



**Figure 6.** EDS Spectrum (a) substrate (soda-lime glass) and deposited film at (b) 400°C; (c) 420°C, (d) 450°C.

### 3.2.3. Electrical Studies

Four point probe technique was used to study the electrical property of the films because of its low demand on sample preparation and high accuracy. The (I-V) characteristic of each film was measured several times with current and voltage drop point swapped in each setting in order to minimize error. The average of the current and voltage values were taken and sheet resistance $R_s$ was calculated using the expression (Schrode, 1998);

$$R_s = \frac{\pi}{In2}\left(\frac{V}{I}\right) \quad (1)$$

Table 1 shows the results of average electrical resistivity, average electrical conductivity and average sheet resistance which were determined for TiN thin films of different thicknesses and deposition temperature. The sheet resistance of the films at different deposition temperature is of the same order, varied in thickness and deposition temperature, this can be attributed to phase transition in a nitrogen environment as reported earlier (Leeward, et al., 2005). The film resistivity decreases might also relate to a reduction in oxygen incorporation at different deposition temperature and non-stoichiometry of the films.

### 3.2.4. Optical Characterization

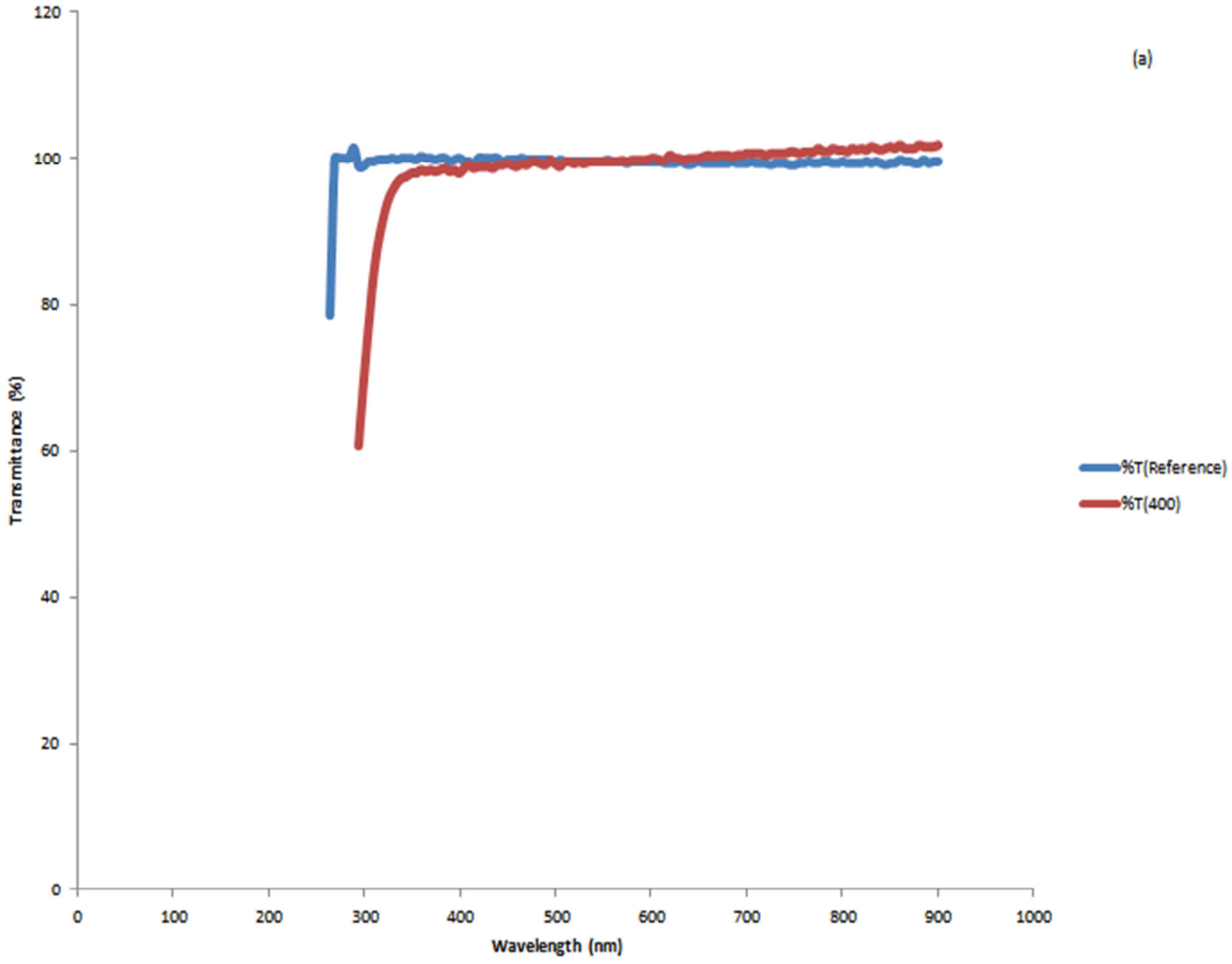
Optical transparency is closely related to surface roughness of the as deposited TiN thin films varied with deposition temperature. Transmission spectra show non-compact films, having a rough and porous surface in relation to SEM image in Figure (4) above. The allowed energy band gap of the films was determined by applying the optical transmission spectra over a range of 200–1100 nm using the Tauc's relationship for the absorption coefficient, α in equation (2) below (Chopra, et al., 1982);

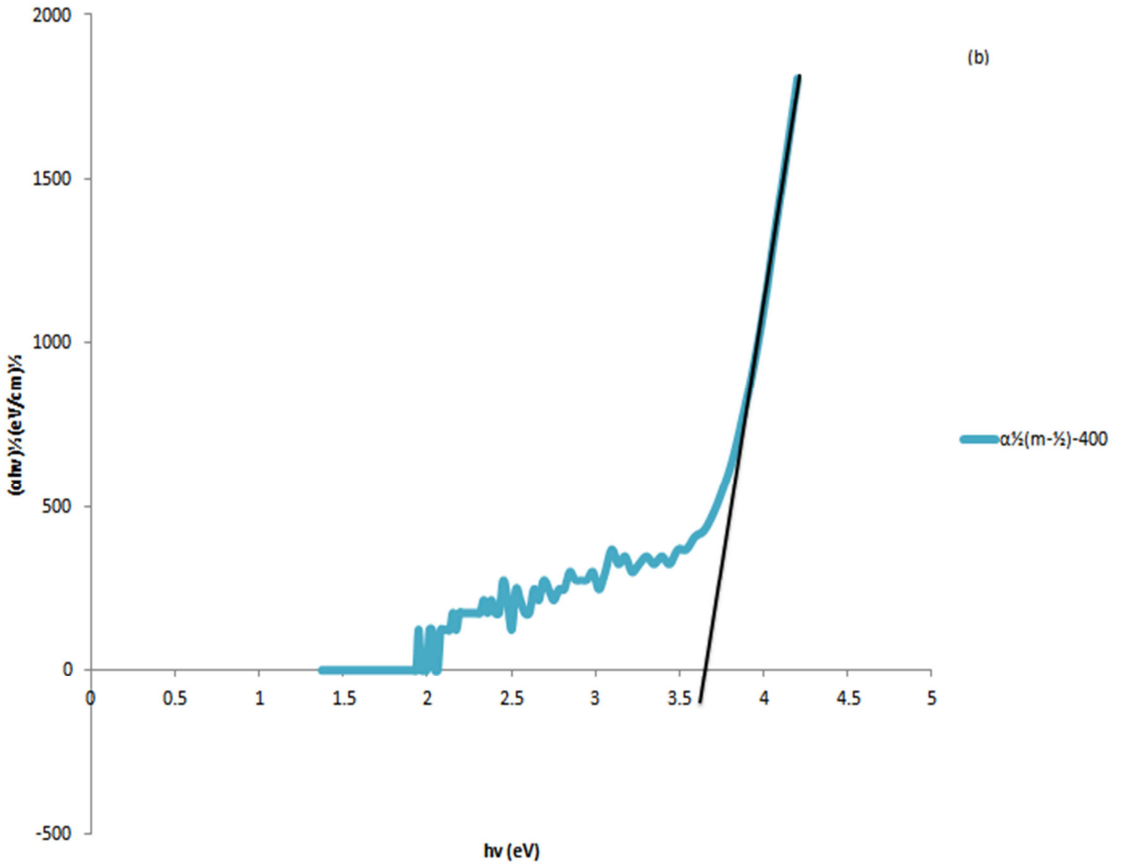
$$\alpha h\upsilon = A_i (h\upsilon - E_g)^m \quad (2)$$

Where $A_i$ is constant and has different values for different transitions, $E_g$ is the energy gap, $hv$ is the photon energy and m is an exponential constant which assume the values 2, ½, 3/2 and 3 depends on the optical electronic transition.

The optical spectra at figure 7(a), 7 (c) and 7(e) show nearly the same transmittance except for a displacement of the absorption edge towards the visible region. The films were high transmittance (>90%) without interference fringes within the visible region so it can be applied as antireflection coating. Increase in substrate temperature leads to decrease in number of free electrons of metal which responsible for the increase in the peak transmittance (due to decrease in the reflectivity and nearly zero at a high electron concentration of the films) (Stephen, 1998). The spectra edge of the films varied as higher energy which corresponds to an inter-band transition with charge transfer excitation, thus it signifies non-stoichiometry as substrate temperature increased lead to varied energy band gaps (Kiran, et al., 2008).

Due to thin film's temperature-independent from transmittance spectra, as explained by Hong et al., (Hong, et al., 1997), the optical energy gap of the film was determined by assuming direct transition replacing $n = 1/m$ which are $n = 2$ (Pankove, 1971) and interpolating the linear fit of the plot $(\alpha hv)^{½} = 0$ of the graph $(\alpha hv)^n$ versus $hv$ as shown in Figure 6. The estimated results reveal that the band gaps fall within 3.62 and 3.68 eV as shown in Table (1). Close examination reveals that the energy gap decreased with deposition temperature. The higher energy may be attributed to the amorphous nature of the films in agreement with published literature (Hem'andez-Rodr'iguez, et al., 2009) and it also shows that the materials can be used in high temperature and power switching applications (Randall, 1999).

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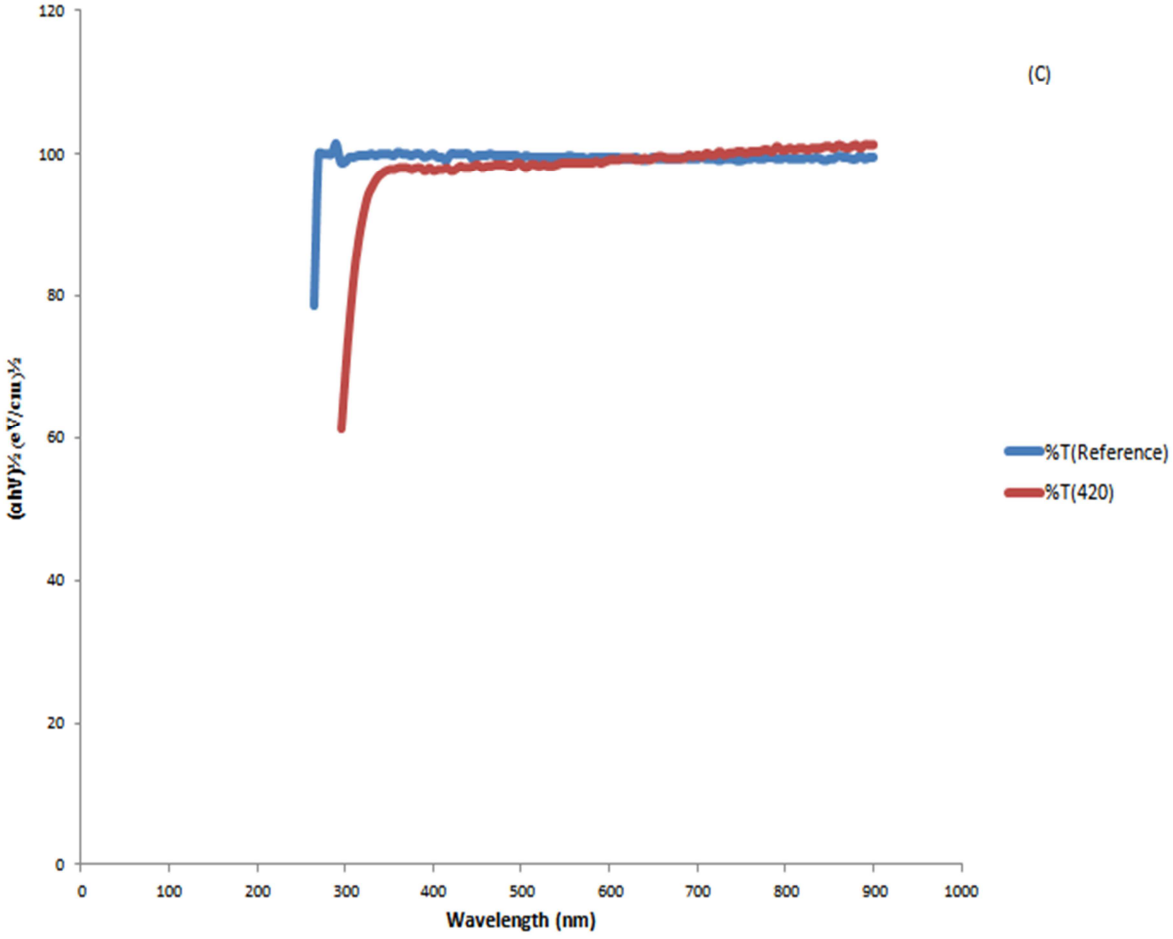
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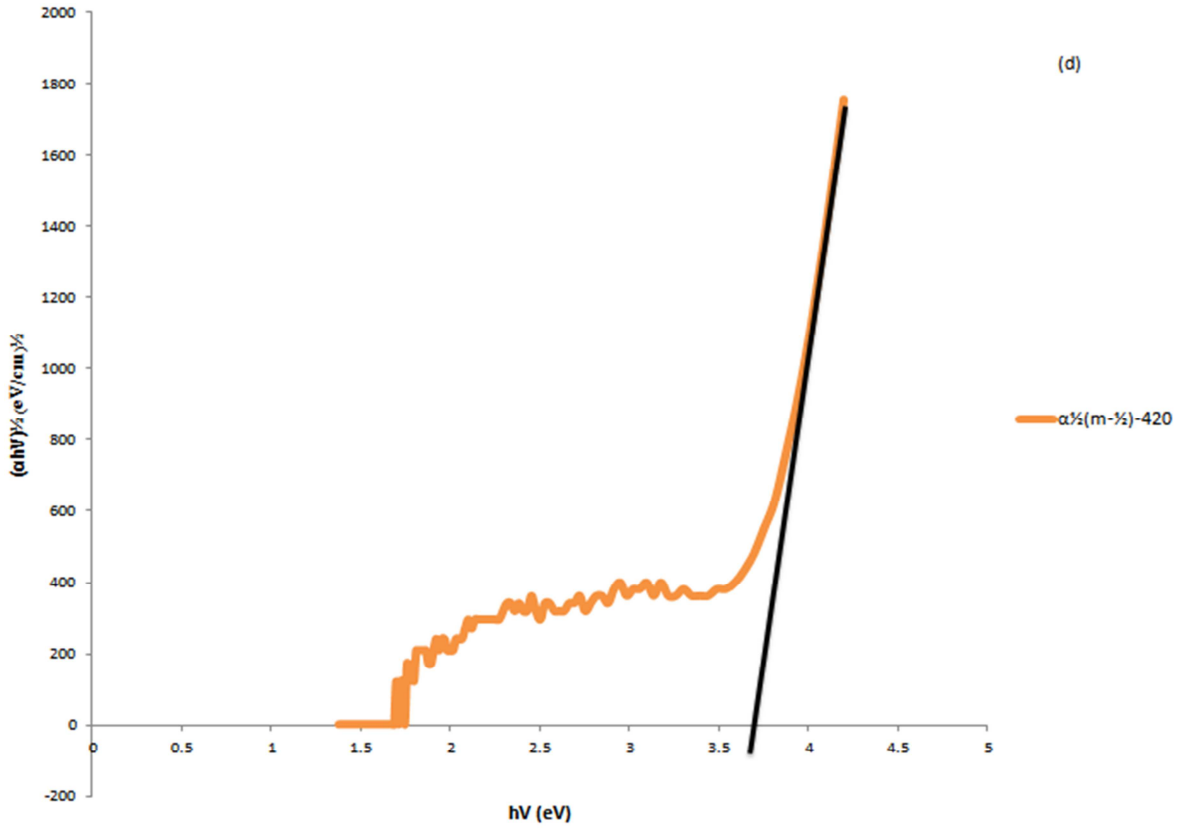
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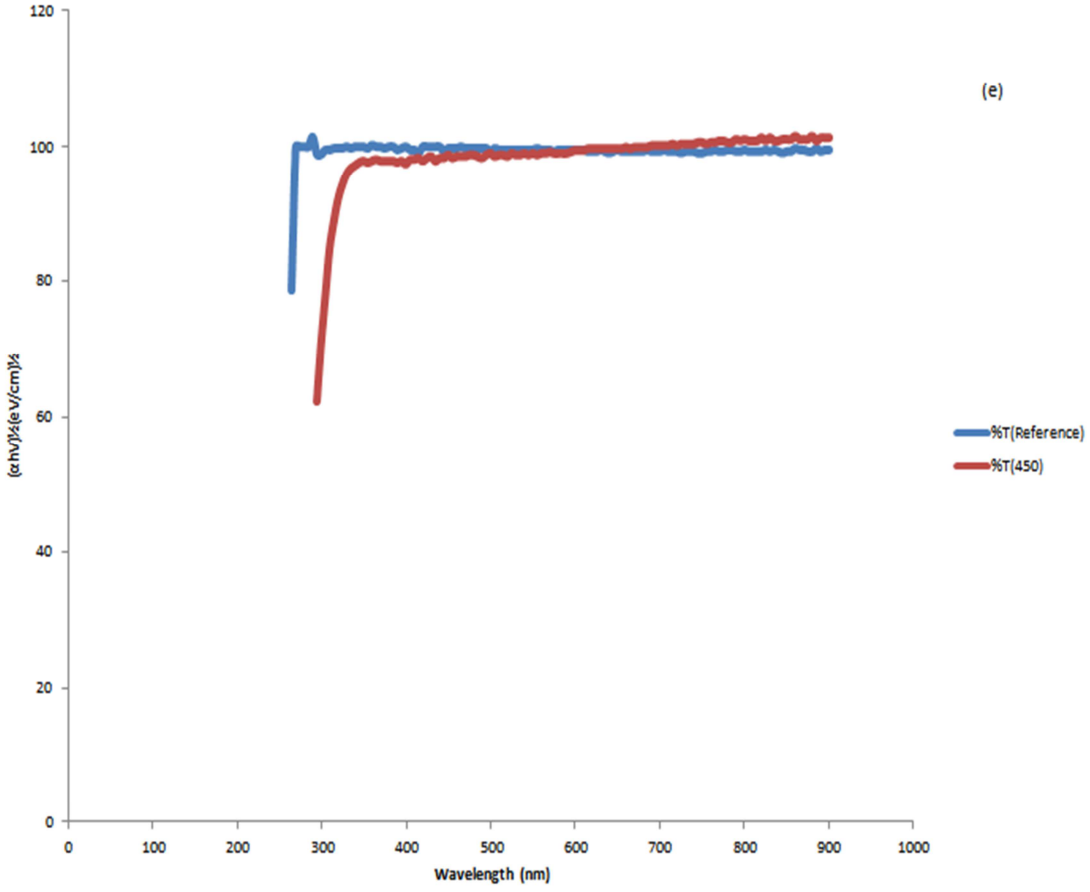
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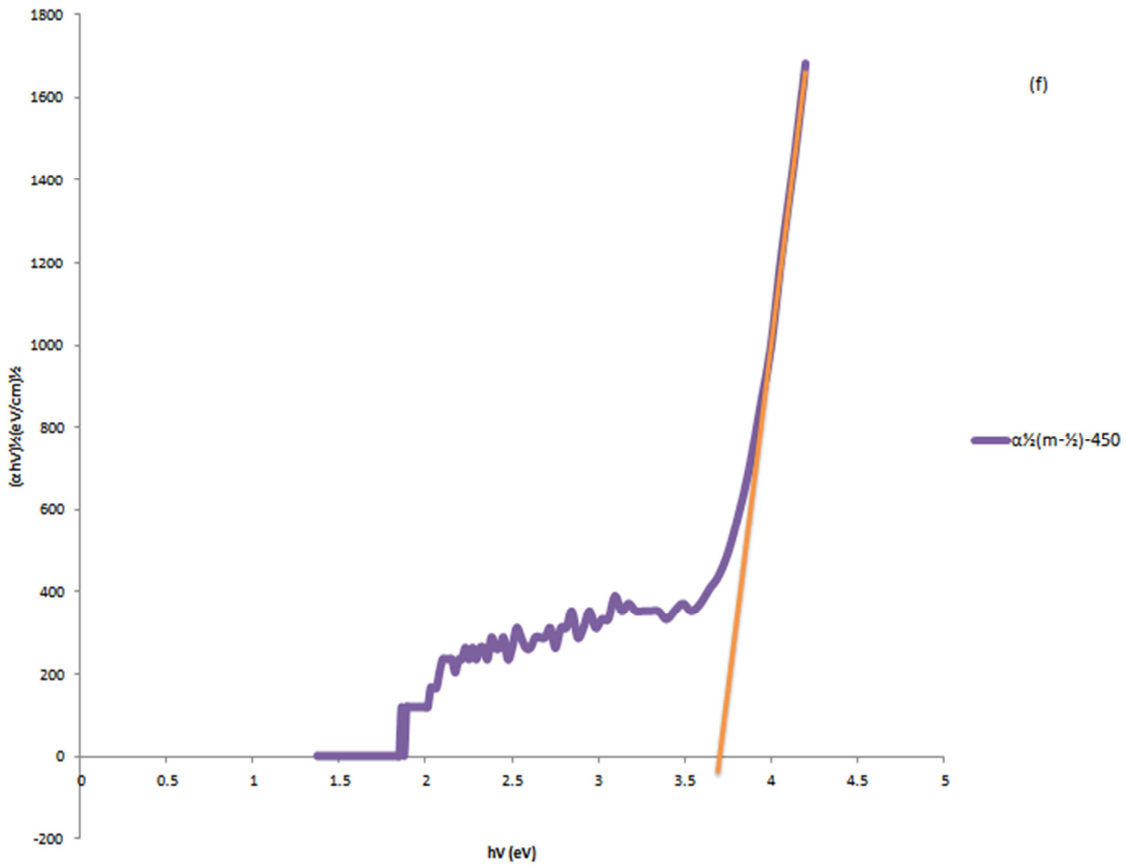


**Figure 7.** Plot of optical transmission spectra (%) and energy band gap of TiN films at 400C, 420C and 450C respectively.

**Table 1.** Thickness, band gap, sheet resistance, resistivity and conductivity of the films deposited at various temperatures.

| Deposition Temperature (°C) | Thickness (nm) | Nitrogen Atomic (%) Proportion | Band Gap (eV) | Average Sheet Resistance (Ω/sq) | Average Sheet Resistivity (Ωcm) | Average Sheet Conductivity ($\Omega^{-1}cm^{-1}$) |
|---|---|---|---|---|---|---|
| 400°C | 152.08 | 46.00 | 3.68 | 10.23 | 1.65 | 0.61 |
| 420°C | 159.67 | 48.50 | 3.65 | 9.92 | 1.58 | 0.63 |
| 450°C | 167.29 | 52.00 | 3.62 | 10.81 | 1.81 | 0.55 |

## 4. Conclusion

The present work demonstrates the possibility of preparing good quality (homogeneous, adherent, specular and fairly smooth) TiN thin film from ethylenediamine based precursor by MOCVD between 400°C and 450°C. The relative thermal stabilities of the single source metal organic precursor of Ti and N elements were achieved, which makes them useful and suitable for industrial applications. Non-stoichiometry (Ti/N ratio) and morphological properties of the films whose optical properties it thus altered showed a strong dependence on deposition temperature. The different thickness presented different colors of the films increased with deposition temperature. (I-V) measurement shows the ohmic nature of the film. The correlations between the structural and optical properties of deposit films established in a consistent manner using SEM, spectral transmittance and surface resistivity indicate that TiN films from single source precursor using MOCVD technique has emerged as a versatile and flexible when compared to other variants of deposition, which makes it possible to obtain high quality films of the desired compound. Finally, the calculated optical gaps, the order of magnitude of the surface resistivity and the possibility to prepare thin films of these materials suggest that, it may be possible to apply them for preparing high temperature electronic device and protecting layer.

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