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PREPARATION AND PROPERTIES OF ELECTROCHROMIC WINDOW COATING BY THE SOL-GEL METHOD

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졸-겔 방법에 의한 전기적 착색 박막의 제작과 특성

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ABSTRACT

Multilayer coatings of WO_3 were deposited by the sol-gel technique on microscope slide glass and ITO coated glass.

These films were characterized optically, chemically, and structurally by XRD, spectrophotometry, DTA/TGA, SEM/EDAX and RBS.

Uniform WO_3 sol-gel films were dip coated on slide glass at dipping speed of 5mm/s. This sample indicated a low near IR transmittance in optical properties as a result of coloration using a dilute HCI electrolyte as the H^+ ion sources. Differential thermal analysis results have allowed the accurate determination of the formation temperature of the WO_3 crystalline phase from the gel data in the range of 380℃−500℃, consistent with crystallization temperature of sol-gel film. RBS spectrometry was performed on the uncolored WO_3 sol-gel film, yielding a chemical composition of WO_3.

요 약

졸-겔 기술에 의해 WO_3 다층박막이 유리와 ITO coated glass 위에 증착되었다. 특성은 XRD, 분광광도계, DTA/TGA, SEM/EDAX 그리고 RBS에 의해서 분석되었다.

균질한 WO_3막은 유리기판위에 dipping 속도 5mm/s에서 증착 되었으며 이 시료는 희석된 HCI 전해액을 사용하여 착색시킨 결과 낮은 근적외선 투과율을 나타내었다.

DTA 결과 380°-500℃ 범위의 gel data는 WO_3의 결정화 온도 형성을 결정하였으며 이 측정치는 졸-겔 박막의 결정화 온도와 일치하였다.

RBS에 의해 착색되지 않은 WO_3 졸-겔 막의 화학조성은 WO_3였다.

1. Introduction

Since Deb's experiments in 1973 on the electrochromism[1], many electrochromic materials (based on WO_3, MoO_3, NiO,etc.) have been investigated using processes such as sputtering, chemical vapor deposition, anodization and evaporation [2-10]

Among the electrochromic materials WO_3 thin film is being investigated widely due to its applicability in "smart windows", allowing dynamic control of the solar energy passing th-rough them[11,12]

More recently, many efforts have been focused on improving the preparation method of electrochromic WO_3 thin film. However, these preparation methods are not suitable for deposition of large-scale samples.

Moreover, since WO_3 exhibits very different eletrical and optical properties depending on deposition technique, and deposition parameters, it is very difficult to optimize the deposition method.

The sol-gel process offers an new approach to deposition of large-scale WO_3 coating optimized for commercial applications. In such a process molecular precursors are transformed into an oxide network by inorganic polymerization reactions. The molecular precursor is usually a metal alkoxide in a suitable organic solvent and polymerization occurs by hydrolysis and condensation [13-14].

In this study, multilayer coatings of WO_3 on microscope slide glass and ITO coated glass substrates were deposited by the sol-gel technique in order to improve the preparation method. The corresponding film properties are discussed herein.

2. Experimental

2.1 Sample preparation.

WO_3 sol-gel films (size : 2.5cm×4cm)were multicoated (5 dip coats) on microscope slide glass and ITO coated glass using a tungsten alkoxide type solution [Tungsten oxy-tetra -n-butoxide$(W^{VI}O^{n}Bt)_4$ in ethanol] by the dip coating technique employing a motor-driven dip coating unit.

Sample preparation method by the sol-gel process for deposition involved four steps. These steps were : coating, drying, hydrolysis, and firing. All samples were coated using various deposition conditions to provide uniform optical properties as well as color in films.

The coating procedure was carried out in a N_2 atmosphere dried using drying materials to protect the solution from deterioration. It is important that the dipping speed(rate of withdrawal from the the solution) be kept as constant as possible during the coating process as variations in produce irregularities in the thickness of the films.

The second stage of the process was the drying of the film to remove excess organic solvent. This was also carried out in a dry N_2 atmosphere to prevent premature contact of the film

with moisture that would lead to the gellation stage of the process. Hydrolysis of the film before solvent evaporation causes cracking of the film. It was found that a minimum of 30 minutes in this N_2 atmosphere was enough to complete this stage.

The third stage involved the introduction of the sample into the air atmosphere. A minimum of one hour was typically allowed for film to hydrolyze and form a gel

The fourth stage of the process was the firing to form a dense film. The firing schedule involved two heat treatments. These were determined by the DTA results. For multiple dip coatings were deposited on the substrates only the first heat treatment of the firing schedule was carried out after each coat. Firing through the 2nd heat treatment for crystallization was carried out after the final coat was deposited

The first heat treatment was to hold the sample at 200℃ for a minimum of 30 minutes to allow the residual organics and moisture to volatilise.

The temperature was then raised to the final firing temperature of 430℃ or higher to allow dehydration of the gel, combustion of any remaining organics and finally crystallization.

2.2 Measurements

A sample of the tungsten alkoxide solution was dried under high purity N_2 atmosphere and then hydrolysis in air to form a WO_3 gel. Thermogravimetric analysis(TGA)was used to measure the weight loss of WO_3 gel, and differential thermal analysis(DTA) (Stanton & Redcroft model STA 780) was also used to measure the energy of transition of bulk WO_3 gels as a function of temperature at a heating rate of 20℃/min in air.

Spectral transmittance of the WO_3 films prepared were measured using a spectrophotometer(Hitach model U-3400). The crystal structures of the films were investigated by X-ray diffraction(Philips model PW 1729)using Co K_α X-ray(wavelength, 1.789Å)and Ni filter. X-ray diffraction studies revealed that WO_3 films were amorphous. The morphology and chemical composion of the film were observed by scanning electron microscopy/energery dispersive X-ray analysis(SEM/EDAX, JEOL model JSM-35C). The film thickness of weakly absorbing films was calculated for relative evaluation using a technique based only on spectrophotometric transmittance data the details of which were given in an earlier pubilcation[15]. Rutherford backscattering spectrometery(RBS) by using facilities of the CSIRO tandem van de graaf accelerator laboratory in Sydney was performed on the uncolored WO_3 film to analyze the chemical composition and thickness. Experimental conditions were 2 MeV He^{++} with 11.0 μc of total charge, in a vacuum environment of approximately 5.3×10^{-4}Pa.

The electrochemical cell for coloration of WO 3 film consisted of a dilute HCI electrolyte (in water) with Cu counterelectrode. A d.c. power supply was connected between the ITO and Cu counterelectrode.

3. Results and discussion

3.1 Optical properties

Fig. 1 shows the variation in spectral transmittance of WO_3 film coated on microscope slide glass. This sample was deposited at the dipping speed of 5mm/s. Measurement was performed

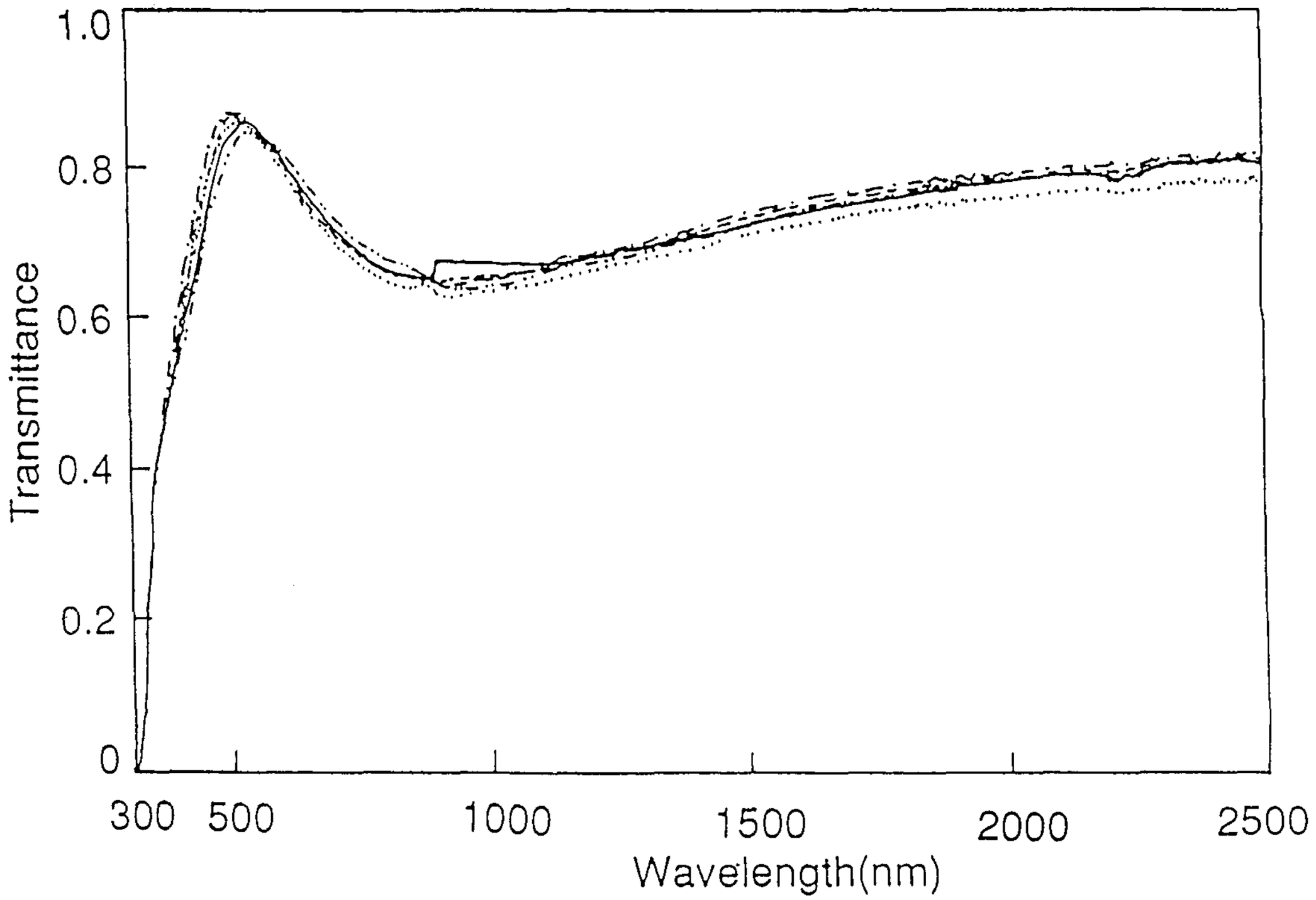

Fig. 1. Spectral transmittance variations in different regions of tungsten oxide sol-gel film coated on microscope slide glass substrate at dipping speed 5mm/s.

on the different positions of sample in order to examine the uniformity. As can be seen in the fig, The transmittance was not changed on the different sample position, and at a photopic wavelength of 550nm, the film showed 85% transmittance. The wavelength of 550mn indicated the peak of the photopic(human eye response spectrum). From this data, it was found that the film was very uniform.

Fig. 2-3 shows the spectal transmittance of coated WO_3 film on slide glass. This sample was deposited at dipping speed of 7.6mm/s-9.8mm/s. Measurement was also done on the different positions of a sample. These results indicated a variation in transmittance with optical thicknes variation. Since color appearance of a sample depends on its absorption character, this transmittance variation means a variation of color. This sample exhibited high variation in transmittance under different thickness in the fig 3. From the data, it is concluded that WO_3 film deposited using a dipping speed of 5mm/s exhibited uniform transmittance characteristics. This is true for colored WO_3 film in regions of uniform thickness.

Table.1 summarizes optical thickness variation of WO_3 sol-gel films calculated in the visible wavelength range. It can be seen that a low dipping speed has a low optical thickness variation.

Fig. 4 shows spectal transmittance of the colored and bleached sol-gel WO_3 films by the

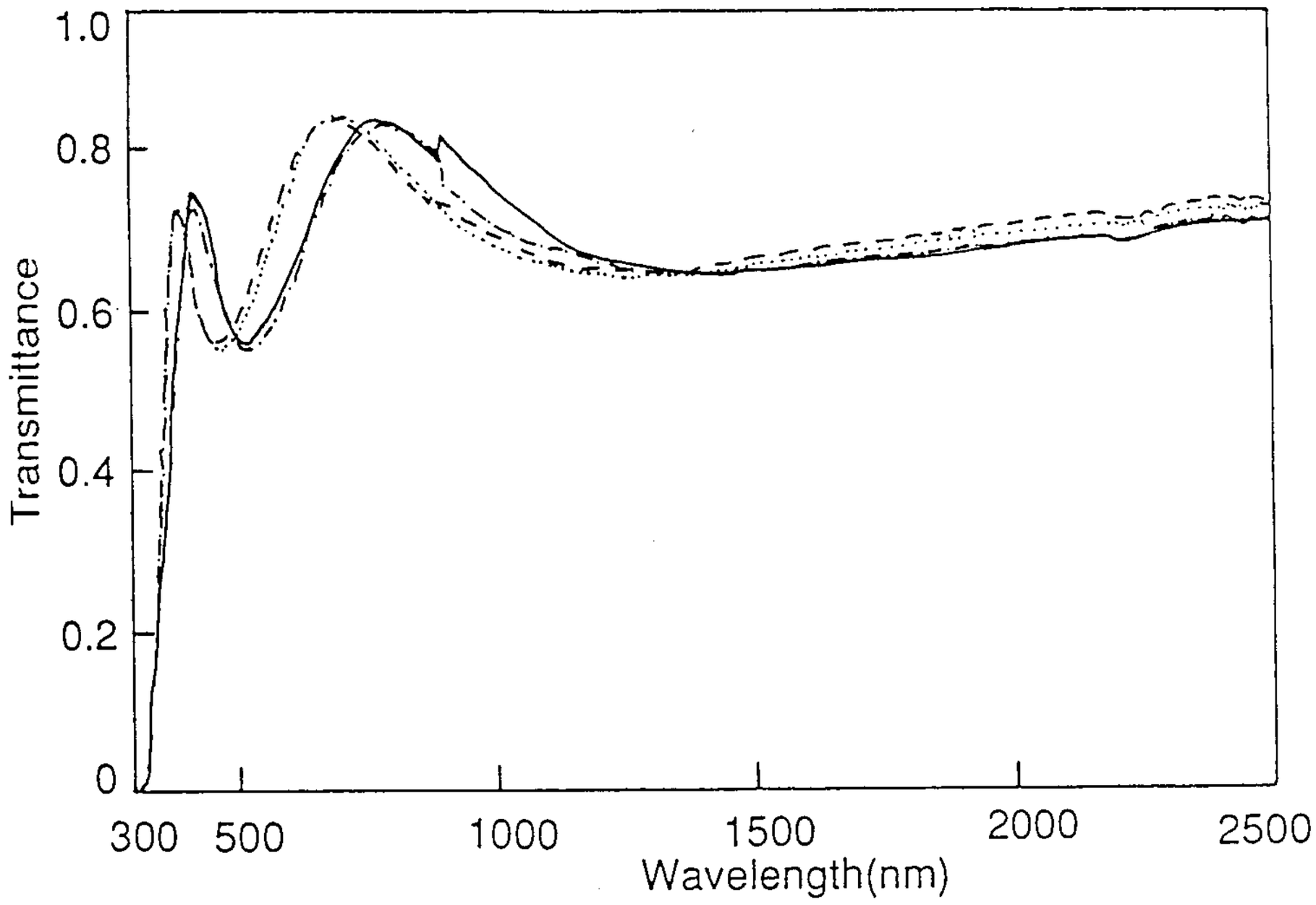

Fig. 2. Spectral transmittance variations in different thickness regions of tungsten oxide sol-gel film coated on glass substrate at dipping speed 7.6 mm/s.

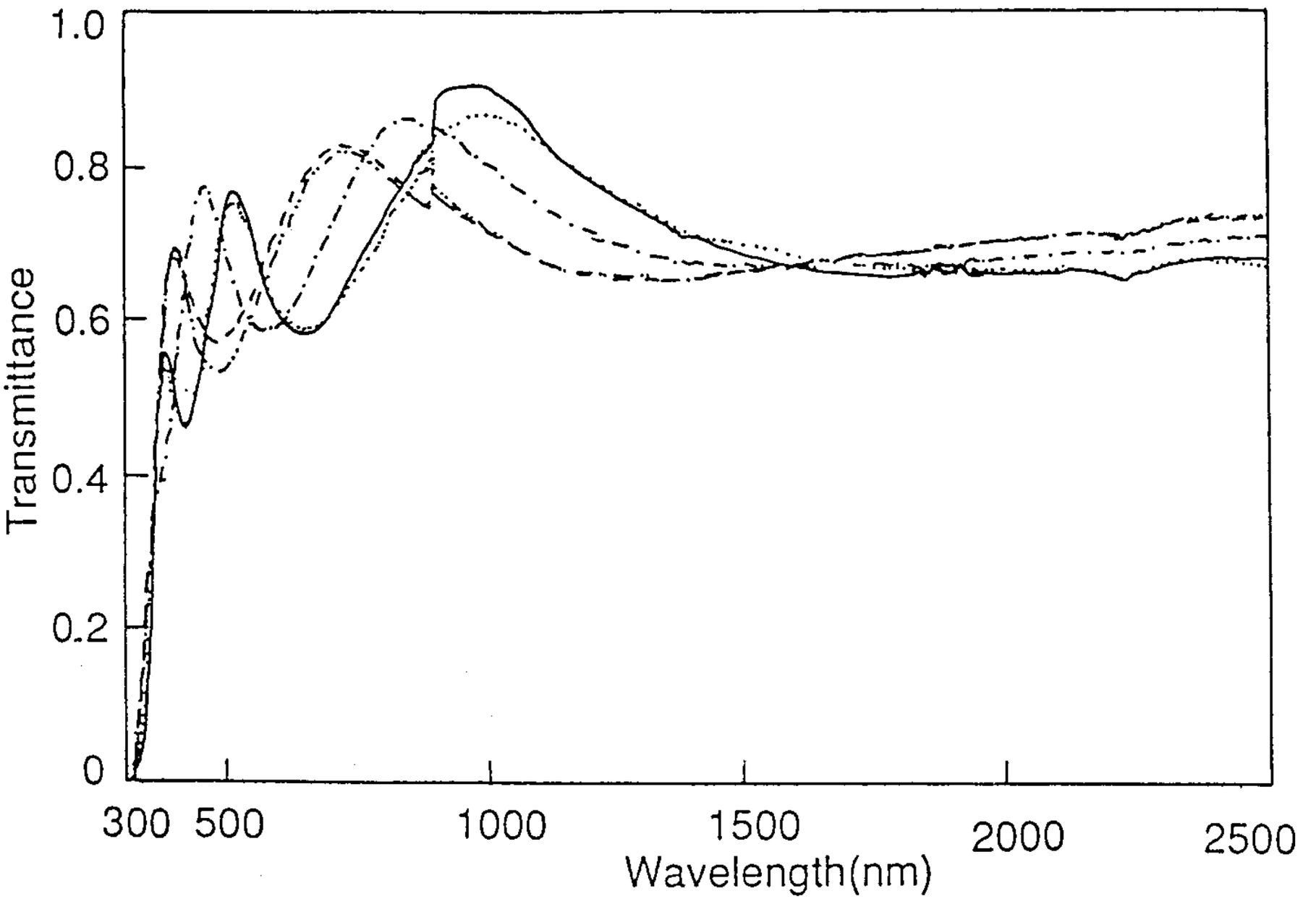

Fig. 3. Spectral transmittance variations in different thickness regions of tungsten oxide sol-gel film coated on glass substrate at dipping speed 9.8 mm/s.

Table 1. Thickness variation with different position regions of the samples.

Uniformity	Dipping speed(mm/s)	Thickness variation(nm)	Firing temp.(℃)
good	5	none	200
bad	7.6	159-185	200
bad	9.8	171-312	200

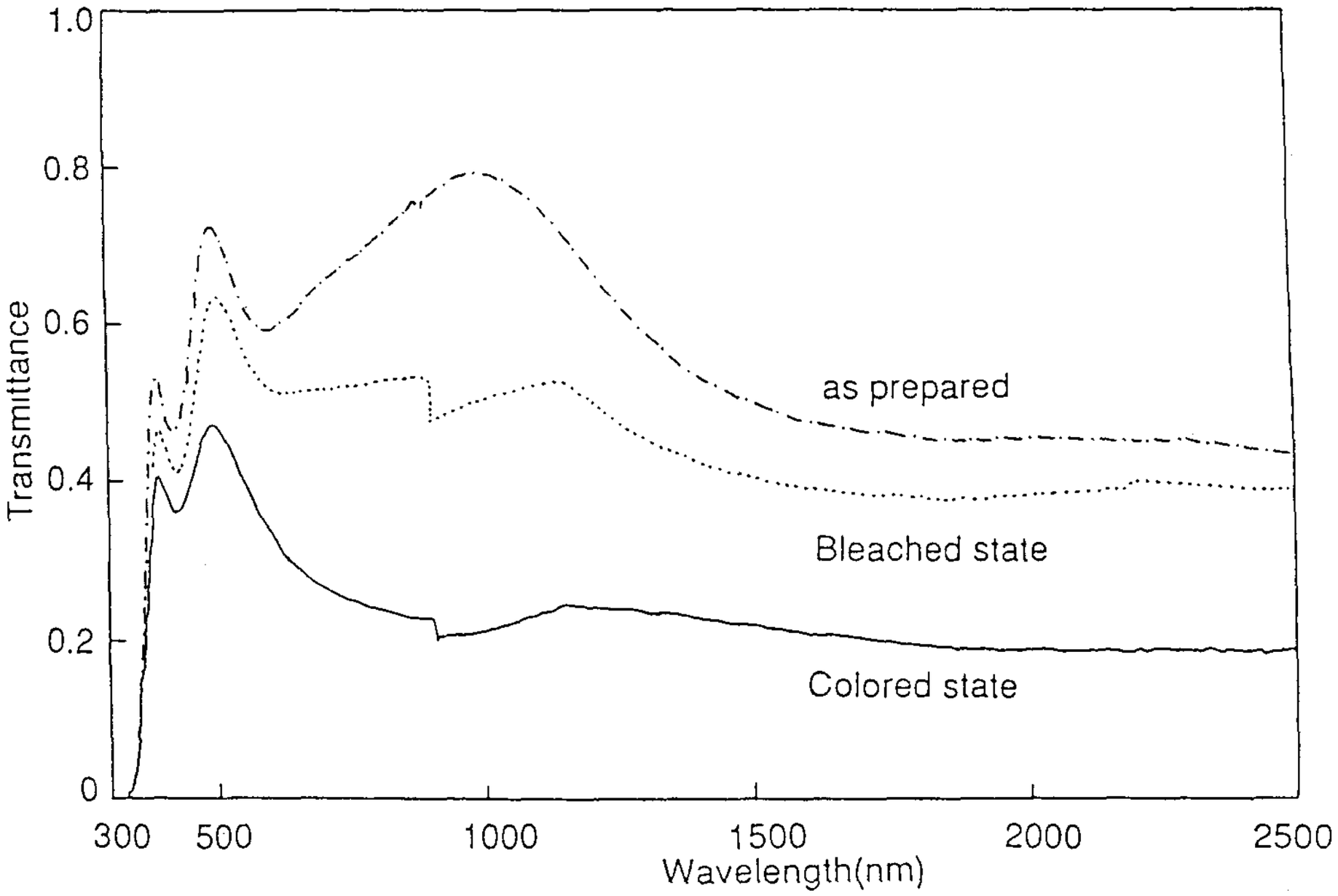

Fig. 4. Spectral transmittance of the tungsten oxide sol-gel film coated on ITO coated glass in colored (applied voltage 1.3V), bleached and as-prepared states.

insertion and extraction of H^+ions. When a d.c. voltage of 1.3V is applied across this cell electron flow occurs through ITO and the WO_3 layer turns deep blue. The coloration remained after the applied voltage was removed. But it does fade.

On reversing the polarity, electrons released by the newly formed cathode may combine with protons in the electrolyte forming H^+ions, allowing the trapped electron in the films to escape to the anode, bleaching the film to its original color. This colored sample indicated low near IR transmittance characteristics. This coloration mechanism could be explained by double injection model[16].

3.2 Structure

Analysis of WO_3 sol-gel film deposited on glass by SEM/EDAX indicated that films deposited at dipping speed of 5mm/s exhibited a very flat surface without pinholes, cracks and metallic contaminants. This indicates that the densification of the coating layers is quite uni-

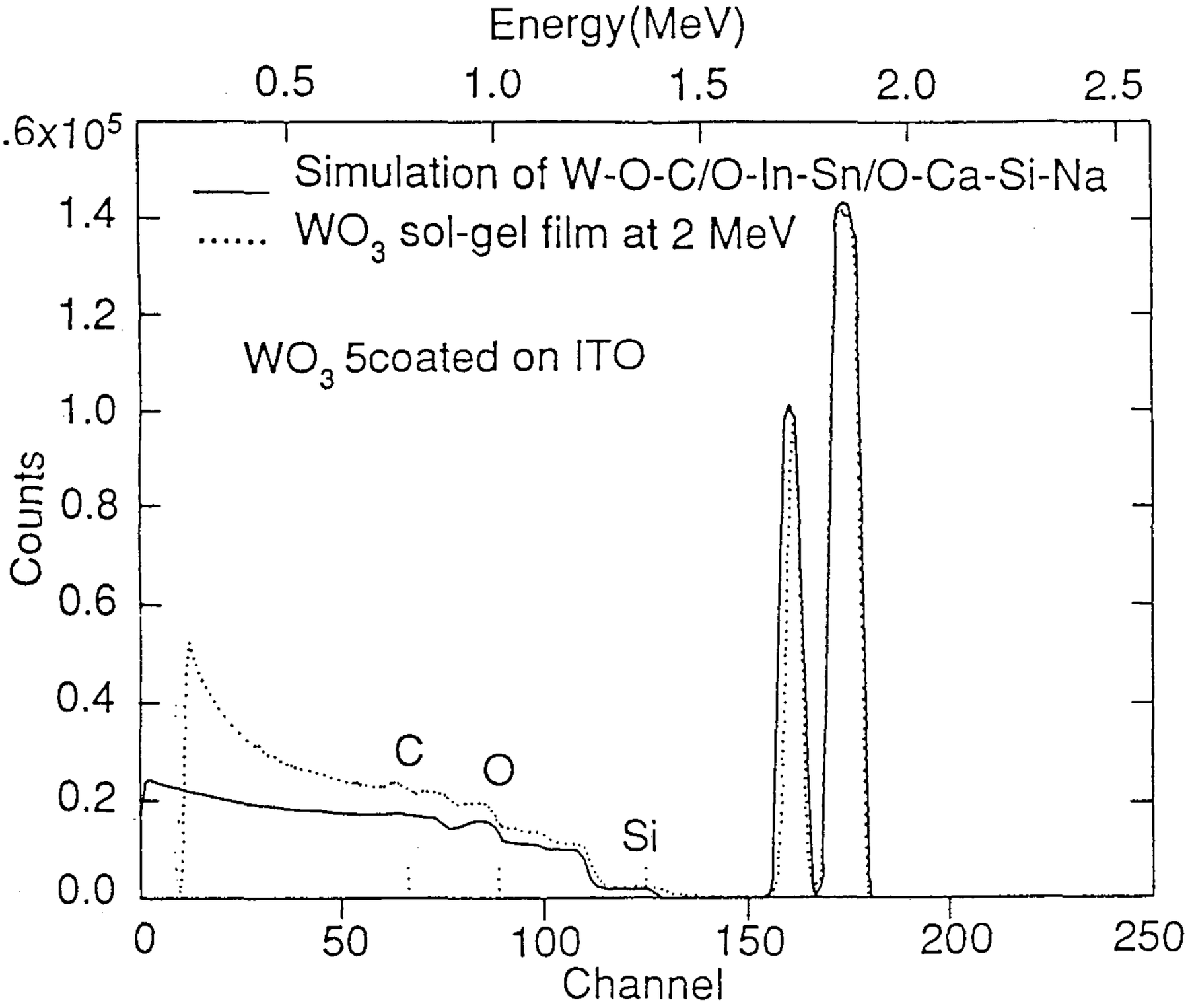

Fig. 5. Rutherford backscattering spectrum of the tungsten oxide sol-gel film coated on ITO coated glass.

Table.2 Summarized results of RBS analysis showing chemical composition and thickness.

Sublayer	Thickness(Å)	Composition
WO_3	700	W : 0.220. O : 0.660. C : 0.120($WO_3C_{0.54}$)
ITO	548.50	O : 0.500, In : 0.400, Sn : 0.050($In_2O_{2.75}$ $Sn_{0.25}$)
Glass	25000.00	O : 0.600. Ca : 0.030. Si : 0.300. Na : 0.070(SiO_2 Ca Na)

form. But deposition conditions had only minor influence on film structure.

Fig. 5 is a RBS spectrum of the uncolored WO_3 sol-gel film on ITO coated glass. The peak at 1.8 MeV corresponds to energy loss of He^{++}ion through the W in WO_3 film. The energy loss is proportional to the thickness of the film and is reflected in the width of the W peak. Assuming WO_3 bulk density of 7.168g/cm^3, this corresponds to a 70nm film with some carbon impurity. Carbon is attributed to ethanol and butanol in WO_3 solution which is not completedly removed during the drying and hydrolysis steps. The integrated area of the same peak is proportional to W content in the film. The width of the W peak is dependent on both the W content and O content of the film, and this leads to a measurement of the film stoichiometry for this particular sample. This data is consistent with stoichiometry of WO_3. The solid line

superimposed over the experimental spectrum represents a computer modeled calculation based on a WO_3 stoichiometry.

Table.2 summarizes results of the composition of the WO_3 sol-gel films on ITO/glass measured by RBS. As seen in the table, the glass substrate was found to contain the elements Si, Ca, O and Na as expected. The film, and the conductive layer, which was composed of $WO_3C_{0.54}$ and $In_2O_{2.75}Sn_{0.25}$, respectively.

3.3 Thermal analysis

Fig. 6 shows the differential thermal and thermogravimetric analysis of a WO_3 gel with a sample weight of 9.5 mg. The first derivative of the thermogram shows peaks at 100℃ and 350℃(DTG graph). The peak indicates that evaporation of solvent and combustion of organic species can be attributed to this weight loss. The DTA/TGA traces show that the sample releases the majority of its hydrocarbon content by 200℃ when it is heated. This implies that heat treatment at higher temperatures only affects the structure and morphology of the films and not the residual organic content(ethanol and butanol). After this there are several stages of rearrangement in the WO_3 gel structure. At approximately 380℃-500℃ there is a small exothermic deak clearly seen in the DTA trace this peak indicates the point at which crystallization WO_3 is taking place.

Fig. 7 shows the X-ray diffraction pattern of WO_3 film coated on slide glass after firing at 430℃, and 530℃.

No diffraction peaks were exhibited for the films heat treated at 200℃, suggesting that amorphism was obtained. Heat treatment to approximately 500℃ produced a structure which was a mixture of several common phases of WO_3.

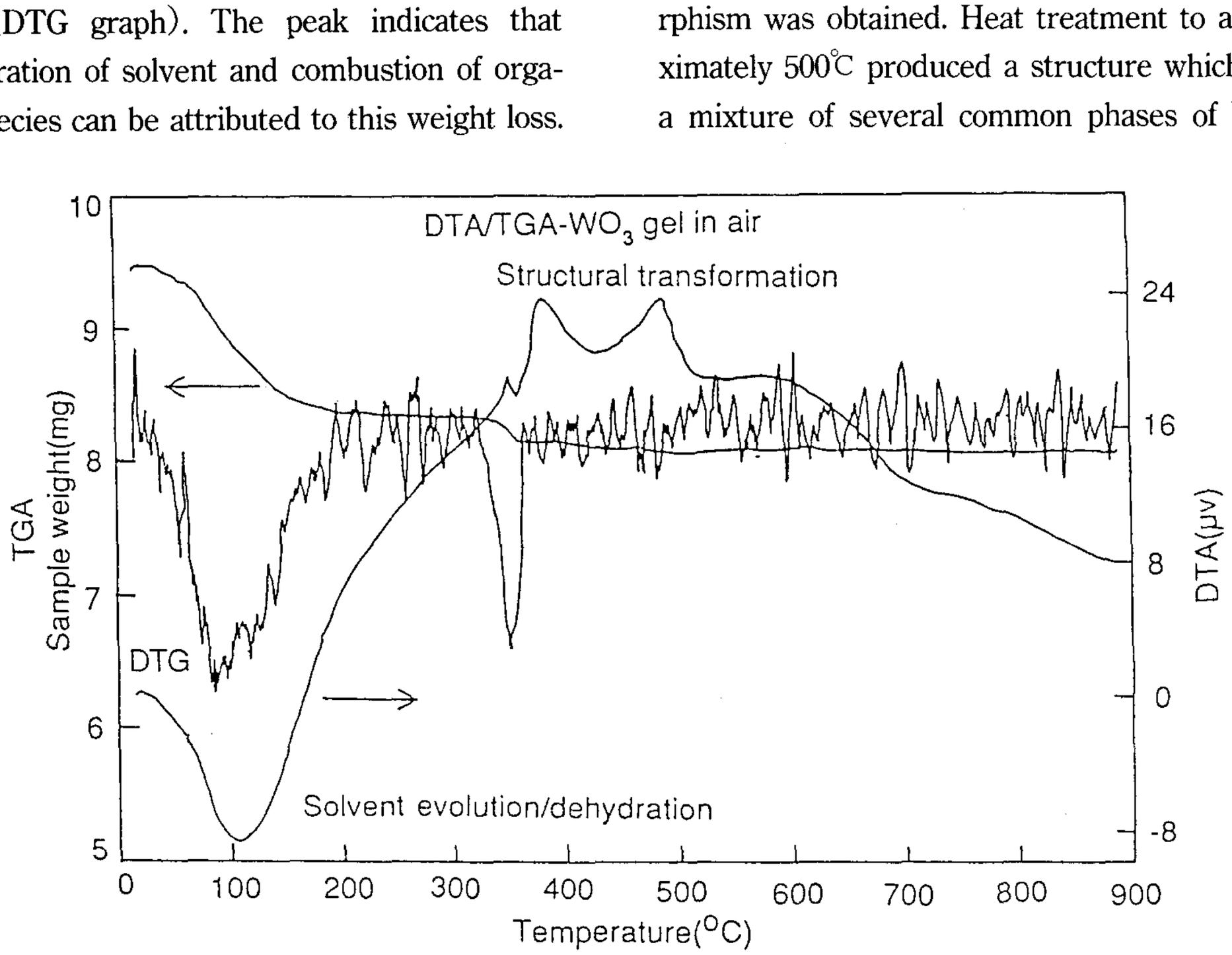

Fig. 6. Differential thermal analysis(DTA) and thermogravimetric analysis(TGA) curves for a dried and hydrolysed tungsten alkoxide solution.

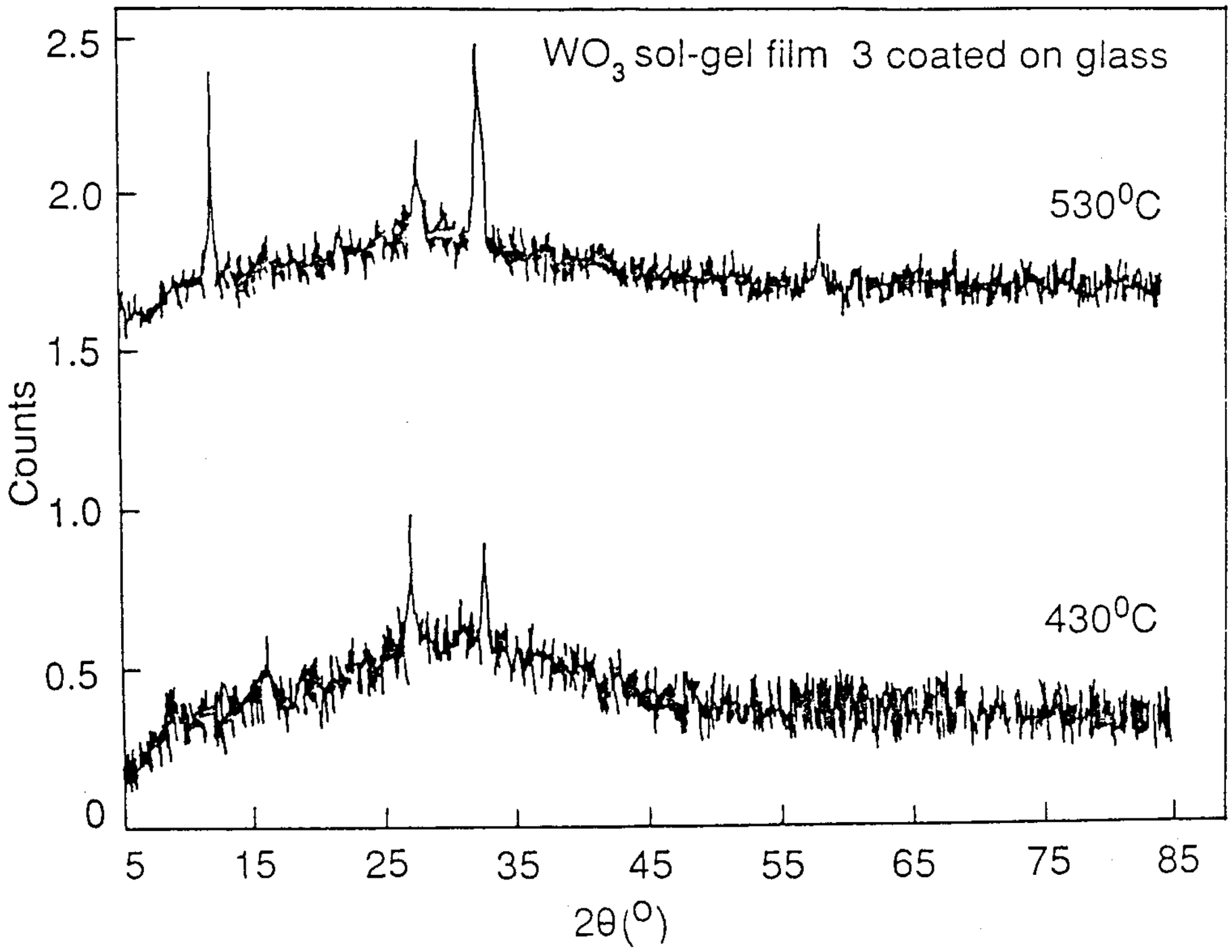

Fig. 7. X-ray diffraction patterns of the tungsten oxide sol-gel film fired at temperatures just above each of the structrual transformation peak shown in Fig 6. The vertical scale are realative to the maximum value of the scan and offset for clarity.

Some regions of these heat treated films also exhibited strong diffraction features which are consistent with regularly spaced defect planes separated by approximately 12Å. This reault confirms identification of formation temperature of WO_3 gel crystalline phase from DTA.

4. Conclusions

Optical properties, structure, thermal analysis, and uniformity of electrochromic WO_3 this film deposited by the sol-gel dip-coating process were investigated. The present results indicate that WO_3 films can be prepared on microscope slide glass substrates with accurate control over the thickness of the films, the degree of crystallinity, and the uniformity of the film.

DTA/TGA analysis results of WO_3 gels have showed an accurate determination of the formation temperature of the WO_3 crystalline phase. By electrochemical and spectrophotometer techniques, WO_3 sol-gel film coated on ITO coated glass showed low near IR transmittance as a result of coloration by the insertion H^+ions.

Thickness and chemical composition of WO_3 sol-gel films coated on ITO were found to be 700Å and WO_3, respectively.

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tube solar collector system. A methanol heat pipe with length of 0.7 m and diameter of 8 ㎜ was manufactured and tested to compare its performance with that of freon thermosyphon which was originally used in a solar collector system fabricated at Thermomax Co..

Then this methanol heat pipe was utilized to be one component, i.e. heat transfer element, of the present experimental model of a solar collector. This model was performed the operation test as its absorber plate was irradiated by infrared lamps.

The following results were obtained.

(1) The methanol heat pipe was showed a stable operation when the variation of axial heat transport was 0~40 watts and that of inclination angle was 30~90°.

(2) The heat transport capability of the heat pipe was proved to be higher than that of the thermosyphon, because the heat transport limitation of the latter was occured at about 30 watt.

(3) The heat pipe in a solar collector was also showed good performance as it transmitted absorbed energy.

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