

Crystal modulation of tungsten oxide gels and films prepared by the sol–gel process using 2,4-pentanedione as an organic ligand

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Tungsten oxide gels and films were prepared by the sol–gel process using 2,4-pentanedione (PTN) as an organic ligand. WO_3 powders were obtained by peeling the films from the quartz glass substrates. The crystal structure of both the gels prepared with and without PTN and fired at 700 °C was monoclinic. WO_3 powders peeled from film samples prepared both with and without PTN showed only the monoclinic crystal structure, whereas the crystal phases of both types of films were cubic and a mixture of cubic and monoclinic crystals, respectively. These results indicate that the cubic crystals of the WO_3 in the films were transformed to the monoclinic crystals of the powders after the films were peeled from the quartz glass substrates. It is concluded that the cubic crystals in the films are transformed to stable monoclinic crystals by the peeling process, whereas PTN and the quartz glass substrate can control the crystal phase of WO_3 films selectively to form the cubic structure.

1. Introduction

Tungsten oxide films are of considerable interest for application as the active layers of electrochromic window devices [1, 2]. These films have been prepared by sol–gel processes as well as by sputtering and evaporation techniques. In the sol–gel process, the films have been prepared from a number of precursors, such as colloidal tungstic solutions [3, 4], tungsten alkoxides [5–8] and tungsten chlorides [9, 10]. Among these starting materials, tungsten chlorides have an advantage because of their low cost.

Tungsten oxide exists in many polymorphic modifications [14, 15]. The literature, however, includes only a few reports of studies concerning the crystal structures of tungsten oxide gels and films prepared by sol–gel processes [9, 14].

A complexing agent-assisted sol–gel process has been proposed as one type of advanced sol–gel process [16–18]. This process tailors the structure or properties of ceramics using an organic ligand as a modulator. We have reported that the organic ligand in the sol–gel process can control the crystal phase and refractive indices of TiO_2 films [17], and the crystal structure of TiO_2 in TiO_2 – SiO_2 (Ti:Si = 50: 50 mol %) [18].

This paper describes the crystal structures of tungsten oxide gels and films obtained by the sol–gel process using 2,4-pentanedione (PTN) as an organic ligand. The transformation of the structure of the WO_3 powders peeled from the film samples is also discussed.

2. Experimental procedure

2.1. The sol–gel process

The preparation of tungsten oxide sols and gels, and the coating process were carried out under an argon atmosphere. A sol with a ligand was prepared at room temperature as follows. Tungsten hexachloride (1 g) was dissolved in ethanol (10 ml), which was dried with molecular sieves and degassed with argon gas bubbling before use. The colour of the solution turned blue. When 2,4-pentanedione (PTN) was added to the blue solution, the solution turned deep green. After allowing the solution to stand for 2 h, H_2O (0.05 ml) was added to the solution, which turned the colour deep blue. The solution was then left standing for over 12 h. A gel was obtained by evaporating the solvent at room temperature. Films were dip-coated on quartz glass substrates in an argon atmosphere, followed by firing in air at temperatures from 300–700 °C. A WO_3 powder was obtained by peeling the film fired at 700 °C from the substrate. The sol, gel, films and powder without a ligand were prepared by a similar process.

2.2. Measurement

The crystal structure of the gels, films and powders was determined by X-ray diffraction (XRD) spectroscopy with a Mac Science MXP3 using graphite-filtered CuK_α radiation. The film thickness was measured using a DEKTAK 3030 stylus profilometer.

3. Results and discussion

3.1. Crystal structure of tungsten oxide gels

The crystal structures of both the gels prepared with and without PTN was determined by XRD by measuring the X-ray intensity as the temperature of the samples was increased at $10\text{ }^{\circ}\text{C min}^{-1}$ under an air flow rate of 200 ml min^{-1} . Both the tungsten oxide gels with and without PTN showed a similar temperature profile. No apparent peak appeared in the region measured here, when the gels were fired at $300\text{ }^{\circ}\text{C}$. However, both type of gels showed peaks when fired at $500\text{ }^{\circ}\text{C}$, and the peak intensity increased as the temperature was raised from $500\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$. These results indicate that the tungsten oxides were amorphous in both types of gel when fired at temperatures up to $300\text{ }^{\circ}\text{C}$ and crystallized at temperatures between 300 and $500\text{ }^{\circ}\text{C}$.

The XRD spectra of both types of gel fired at $700\text{ }^{\circ}\text{C}$ were also measured at room temperature. The XRD patterns of the gels were similar, and were also similar to those measured at $700\text{ }^{\circ}\text{C}$. Fig. 1 shows a typical XRD pattern measured at room temperature for a tungsten oxide gel that was prepared with PTN and fired at $700\text{ }^{\circ}\text{C}$. The pattern is complicated and three large peaks are observed in the 20° – 25° region.

Tungsten oxides exhibit many crystal modulations and display characteristic XRD profiles corresponding to the different crystal structures [14, 19, 23–25]. The monoclinic structure [24] characteristically shows three large peaks in the 20° – 25° region and d values of 0.3769 , 0.3648 and 0.3384 nm . The peak profile is also more complicated than that of the cubic [14] and tetragonal [25] WO_3 crystal structures, but is similar to that of the triclinic [19] and orthorhombic [23] structures. On the other hand, the cubic structure shows the simplest peak profile of all the WO_3 crystal structures; it typically shows one large (100) peak at a $d = 0.371\text{ nm}$ for the powder [14] and $d = 0.3833\text{ nm}$ for the film [26].

Both the gels prepared with and without PTN are ascribed to the monoclinic structure because the XRD pattern in Fig. 1 is similar to the monoclinic one [24]. The lattice constants of both types of gel were calculated using the XRD patterns of the gels fired at $700\text{ }^{\circ}\text{C}$, and are listed in Table I. The lattice constants

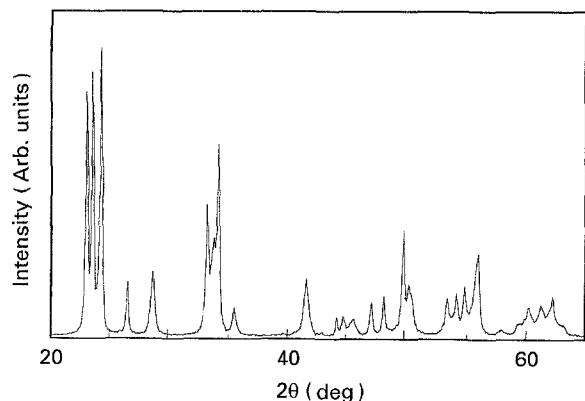


Figure 1 XRD pattern of a tungsten oxide gel prepared with PTN and fired at $700\text{ }^{\circ}\text{C}$.

TABLE I Lattice constants of the WO_3 gels, films, and powders

Samples	Lattice constants (nm)	
	With PTN	Without PTN
Gels	$a = 0.730$ $b = 0.756$ $c = 0.770$ $\beta = 90.4^{\circ}$	$a = 0.730$ $b = 0.754$ $c = 0.771$ $\beta = 90.4^{\circ}$
Films	$a = 0.365$	Not examined
Powders	$a = 0.730$ $b = 0.753$ $c = 0.768$ $\beta = 90.1^{\circ}$	$a = 0.732$ $b = 0.758$ $c = 0.773$ $\beta = 90.3^{\circ}$

of both types of gel are similar to the values reported in the literature [24]: $a = 0.7297\text{ nm}$, $b = 0.7539\text{ nm}$, $c = 0.7688\text{ nm}$ and $\beta = 90.6^{\circ}$. The tungsten oxide gels prepared in this study showed only the monoclinic crystal structure when fired at 500 and $700\text{ }^{\circ}\text{C}$, regardless of whether or not PTN was used. In the gel-preparation process, PTN did not exhibit any selectivity in connection with the crystal formation of WO_3 gels. It is concluded that monoclinic crystals of WO_3 were formed as a stable structure in this sol-gel process.

3.2. Crystal phase of tungsten oxide films

The crystal phase of WO_3 films on quartz glass substrates has been discussed elsewhere [27]. The cubic phase of WO_3 was selectively formed on quartz substrates when PTN was used as the ligand, but a mixture of cubic and monoclinic crystals was formed on quartz glass substrates when PTN was not used [27]. Fig. 2 shows the XRD pattern of a cubic crystal WO_3 film (a) that was prepared with PTN and fired at $700\text{ }^{\circ}\text{C}$, and had a thickness of approximately 200 nm . A large (100) peak is observed at $d = 3.661\text{ nm}$.

The lattice constant of the cubic crystal was calculated using the XRD pattern in Fig. 2 and is listed in Table I. The lattice constant of the film is $a = 0.365\text{ nm}$ which is shorter than that ($a = 0.3714\text{ nm}$) of the cubic WO_3 powder reported in

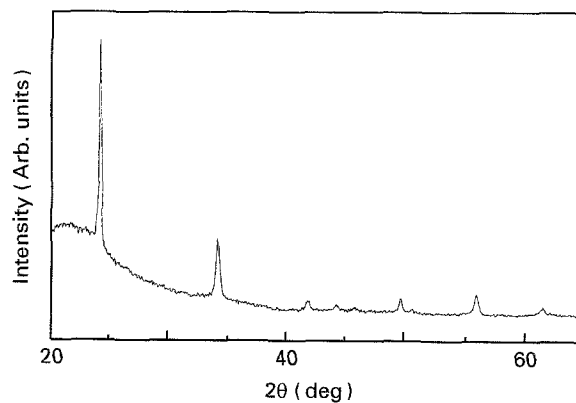


Figure 2 XRD pattern of a WO_3 film (a), which was prepared with PTN and fired at $700\text{ }^{\circ}\text{C}$ and had a thickness of approximately 200 nm .

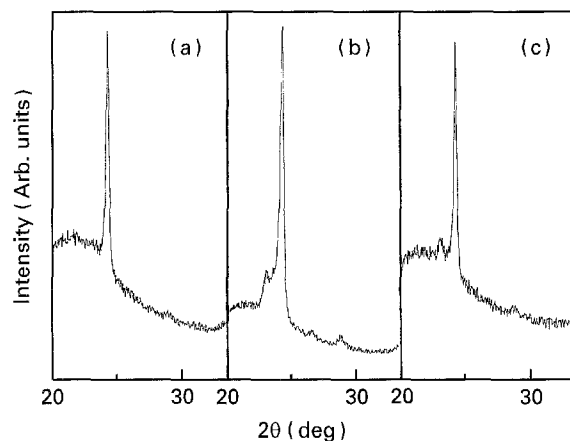


Figure 3 XRD profiles of three WO_3 films in the 20° – 33° region. Films (b) and (c) were approximately 400 nm in thickness, and (b) was prepared by coating the concentrated gel solution once and (c) was prepared by coating the original gel solution twice.

the literature [28]. Some researchers have reported that the XRD patterns of WO_3 films are different from those of the corresponding powders [26, 29, 30]. It is reasonable to consider that the lattice constant of the cubic crystals in the WO_3 film was reduced somewhat by the influence of the quartz glass and PTN.

Two types of thicker films (b) and (c) were formed to a thickness of approximately 400 nm by coating a concentrated gel solution once and the original gel solution twice, respectively. Their crystal phases were determined by XRD spectroscopy at room temperature. The XRD patterns of (b) and (c) were similar to that of (a) except in the 20° – 33° region. Fig. 3 shows the XRD profiles of all three films in this region. Films (b) and (c) show two small peaks and one small peak near the large (100) peak, respectively. These small peaks are hard to attribute to any precise source because of their very small size. However, they are presumed to stem from the monoclinic structure because the gels prepared with PTN are ascribed to be monoclinic. This suggests that the selective formation of the cubic structure is not maintained with a thicker film and when the gel solution was coated twice. Further, it suggests that the tungsten oxides tend to take a stable monoclinic structure when they are far from the surface of the quartz glass, and that the influence of the quartz glass on the crystal structure of tungsten oxides is limited to a narrow region. In fact, the selective formation of the cubic phase was achieved only when the film thickness was less than 200 nm and the coating was performed only once. Accordingly, it is concluded that PTN and the quartz glass substrate work to produce the cubic structure of WO_3 under these conditions.

3.3. Crystal structure of WO_3 powders

A tungsten oxide powder was obtained by peeling the WO_3 film (a), which was prepared with PTN, from the quartz glass substrates. The crystal structure of the powder was determined by XRD spectroscopy within 1 h after the film was peeled. The XRD pattern of the powder shown in Fig. 4 exhibits many peaks in the

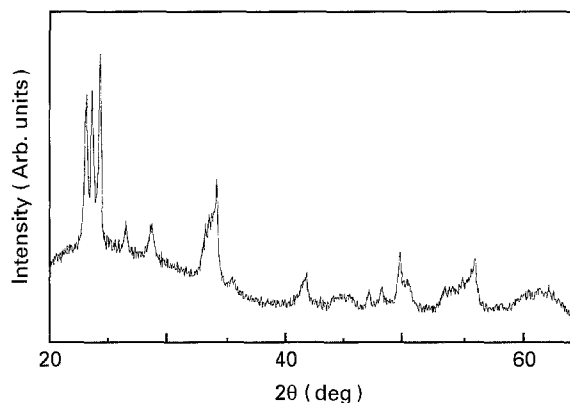


Figure 4 XRD pattern of a powder peeled from a WO_3 film prepared with PTN.

region measured here, and a more complicated pattern than that of the corresponding film (a) (Fig. 2). The pattern does not resemble that of the cubic crystal film (Fig. 2), but is similar to that of the monoclinic crystal (Fig. 1). This result indicates that the powder from the film (a) is monoclinic in structure. The lattice constants of the powder were calculated from the XRD pattern in Fig. 4 and are listed in Table I. The lattice constants of the powder are similar to those of the gel prepared with PTN. These results indicate that the cubic crystals in the WO_3 film prepared with PTN are transformed to monoclinic crystals by the process of peeling the film from the quartz glass substrate.

A powder was also obtained from the film prepared without PTN on quartz glass substrates, and the crystal structure was determined in the same way. The XRD pattern of the powder was similar to that of the powder obtained from the film (a). This result indicates that the crystal structure of the powder is monoclinic, although the crystal phase of the WO_3 film prepared without PTN was a mixture of cubic and monoclinic crystals. Accordingly, the cubic crystals in the film are also transformed to monoclinic ones by the process of peeling the film from the quartz glass substrates.

4. Conclusion

Tungsten oxide gels and films were prepared by the sol-gel process using 2,4-pentanedione (PTN) as an organic ligand, and WO_3 powders were obtained by peeling the films from the quartz glass substrates. The gels crystallized at temperatures between 300 and 500°C . The crystal structure of both the gels prepared with and without PTN and fired at 700°C was monoclinic, and the lattice constants were similar to the values reported in the literature. PTN and the quartz glass substrate worked to produce the cubic crystal structure when the film thickness was less than 200 nm and the coating was performed only once. WO_3 powders peeled from both the films prepared with and without PTN showed only the monoclinic crystal structure, whereas the crystal phases of both types of film were cubic and a mixture of cubic and monoclinic crystals, respectively. These results indicate that the cubic crystals of the WO_3 in the films were

transformed to the monoclinic crystals of the WO_3 powders after the films were peeled from the quartz glass substrates. It is concluded that the crystal structure of the WO_3 gels prepared with and without PTN is monoclinic, whereas PTN and the quartz glass substrate can control the crystal phase of the WO_3 film to form the cubic structure under limited conditions. It is also concluded that the cubic crystals of WO_3 in the film on quartz glass substrate were transformed to stable monoclinic ones by the peeling process.

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Received 1 June 1994
and accepted 11 April 1995