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Thin Solid Films 493 (2005) 301 – 306
thin solid films
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Effects of deposition and annealing atmospheres on phase transition of tungsten oxide films grown by ultra-high-vacuum reactive sputtering

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Received 17 November 2004; received in revised form 16 June 2005; accepted 19 July 2005
Available online 31 August 2005

Abstract

A series of oxygen-contained tungsten films were grown on Si(100) substrates without intentional heating by ultra-high-vacuum reactive magnetron sputtering at a constant argon pressure (P_{Ar}) of 1.33×10^{-1} Pa mixed with a wide range of O_2 partial pressures (P_O) from 1.33×10^{-4} to 4×10^{-1} Pa, equivalent to P_O-to-P_{Ar} ratios ($P_{O/Ar}$) from 1×10^{-3} to 3. The effect of varying $P_{O/Ar}$ on phase evolution was evaluated by annealing the films in a controlled atmosphere (argon or oxygen) at 500 or 700 °C for 1 h. Grazing incident X-ray diffraction and transmission electron microscopy, together with the data of electrical resistivity and deposition rate, reveal that gradually increasing $P_{O/Ar}$ induces a sequence of phase transitions from nanocrystalline β-W(O) ($P_{O/Ar} \leq 0.1$), amorphous WO_2 ($P_{O/Ar}=0.6$) to amorphous WO_3 ($P_{O/Ar} \geq 2$). When annealed in argon atmosphere, the amorphous WO_2 and WO_3 exhibit a very different magnitude of crystallization temperature (T_c) and can be transformed, respectively, into monoclinic WO_2 ($T_c=500$ °C) and tetragonal WO_3 ($T_c=700$ °C). However, the oxidizing atmosphere plays a role to accelerate significantly the crystallization of the amorphous WO_2 into a completely different phase (monoclinic WO_3) at a significantly reduced T_c of 500 °C.
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PACS: 05.70.Fh; 64.60.My; 64.70.-p; 81.15.Cd
Keywords: Sputtering; Sensors; Tungsten oxide; X-ray diffraction

1. Introduction

Tungsten is a very thermally and chemically stable refractory metal that is often grown by sputtering deposition for use as a contact plug or diffusion barrier in integrated circuits [1], or as a seed layer for electrochemical plating [2]. Although the thermodynamically stable form of tungsten is body-centered-cubic α-W, the A15 crystal structure of tungsten films, designated β-W, has been widely observed [3,4]. The residual gases in a deposition atmosphere, especially O_2, markedly accelerate the formation of the highly resistive β-W(O) which is readily to age into α-W [5–10], adversely impacting the stabilities of grain and crystal structures of the tungsten films [10–12]. However, most of the works analyze qualitatively the influence of oxygen among other residual gases on enhancing the formation of the β-phase in the deposited tungsten films [5,7–10,12]. It is thus highly desirable to quantify the impact of oxygen on the phase-forming behavior of tungsten films.

Thin films of tungsten trioxide (WO_3) have received extensive attention owe to the technological importance of this material in the field of electrochromics [13] and gas sensing [14,15]. As is generally known, sputtering a tungsten metallic target using an Ar–O_2 reactive atmosphere is one of the key processes to grow WO_3 films. Inadequate control of the deposition atmosphere usually ends up with the formation of a poorly crystalline, oxygen-deficient tungsten oxide (WO_{3-x}) film with degraded sensing properties. Therefore, a high-temperature annealing treatment, typically from 500 to 700 °C, is normally required to stabilize and crystallize the WO_3 film [16,17],

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0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.07.309

also heightening the importance of adequately controlling (a) the reactive oxygen atmosphere and (b) the condition of the stabilization annealing in fabricating WO_3 gas-sensing films.

The aim of this study is to elucidate the influence of varying the partial-pressure fractions of the Ar–O_2 reactive atmosphere and the conditions of the stabilization (crystallization) annealing on the phase evolution of the W–O films grown by ultra-high-vacuum reactive dc magnetron sputtering. The process window of the deposition atmospheres to grow single phase of metallic W(O) or tungsten oxides (WO_2 and WO_3) will be determined, and the role of the annealing atmosphere (argon or oxygen) to influence the phase-transition behavior and the tendency of forming the highly crystalline WO_2 and WO_3 will also be presented.

2. Experimental details

A series of oxygen-contained tungsten (W–O) thin films were deposited in a reactive sputter magnetron deposition system comprising an ultra-high-vacuum growth chamber with a base pressure of $\sim 1 \times 10^{-7}$ Pa (8×10^{-10} Torr) in conjunction with two stages of load locked chambers with base pressures of 1 Pa and 10^{-5} Pa, respectively. The growth chamber and load locked chambers were evacuated by a 1000 l/s turbo-molecular pump (TV1001 Navigator, Varian, Inc), backed by Varian Triscroll™ 300 dry mechanical pumps, eliminating the oil back-streaming. The flow rate of argon was controlled by a mass flow meter to give a constant deposition pressure (P_{Ar}) of 1.33×10^{-1} Pa. A Granville-Philips ultra-high-vacuum variable leak valve (Series 203) capable of varying the gas throughput continuously over a broad range from 1.33×10^{-11} Pa m^3/s (10^{-10} Torr l/s) to 40 Pa m^3/s was used to admit the O_2 gas over a wide range of working pressures (P_O) from 1.33×10^{-4} Pa to 4 Pa, equivalent to P_O-to-P_{Ar} ratios ($P_{O/Ar}$) from 1×10^{-3} to 3. The pressure was measured by a Granville-Philips 307 modular (Convectron and Bayard-Alpert ionization) vacuum gauge.

All of the thin films were deposited on p-type silicon (100) substrates, placed on an electrical-floated substrate holder (SU-200, US Gun, Inc.) without intentional heating, by reactively sputtering a tungsten target (50 mm in diameter and 99.95% purity) using the Ar–O_2 mixed gases discharged by a dc power of 200 W. The target, 14 cm away from the substrate, was mounted to a chimney and gas-ring equipped ultra-high-vacuum sputter source (A320-U-A, AJA International, Inc.). The thickness of the films was measured ex situ using a high-precision (20 nm ± 3%) step profilometer (ET3000, Kosaka Lab. Ltd.) and ranged from ~60 to ~120 nm. Some of the as-deposited films were annealed in a tube furnace under the atmosphere of 1.5-atm argon (or oxygen) at 500 °C (or 700 °C) for 1 h. Grazing incident (3°) X-ray diffraction with Cu radiation ($\lambda = 0.154$ nm) and transmission electron microscopy (TEM) operated in JEOL 1200 EX II were applied to elucidate the impact of varying the pressure ratios ($P_{O/Ar}$) and the annealing atmospheres on the phase transition of the W–O films. The magnitudes of sheet resistivity of the films were obtained using a four-point probe meter. Resistivity of the films, procured from film thickness and sheet resistivity, was also used to provide additional evidence for phase identification. To prevent phase change by the room-temperature aging [12], all analyses were made immediately after film deposition.

3. Results and discussion

Fig. 1 displays a series of XRD patterns for the films deposited at a constant P_{Ar} of 1.33×10^{-1} Pa mixed with a wide range of oxygen partial pressures (P_O) from 1.33×10^{-4} to 4×10^{-1} Pa, equivalent to $P_{O/Ar}$ from 1×10^{-3} to ~3. Identifying the sharply defined peaks in Fig. 1a, b and c with the source data [18] confirms that the films deposited at the low $P_{O/Ar}$ regime (1×10^{-3}–0.1) are highly crystalline, metallic A15 β-W(O) phase. The gradual shift of these peaks, obviously seen in the low-angle reflections, toward the left following the increase of P_O indicates that increasing the amount of the incorporated oxygen expands the lattice monotonically. This expansion is accompanied by a gradual loss of the peak profiles, implying that the burial oxygen tends to cause the films to lose their crystalline identity. Hence, poorly defined patterns were observed at the high regime of $P_{O/Ar}$ from 0.2 to ~3 (Fig. 1d, e, f and g), generally interpreted as the W–O films being with an amorphous structure [13,19–21].

To characterize the phase distribution, the films grown at the high $P_{O/Ar}$ regime (0.2–3) were annealed at 500 °C (or 700 °C) for 1 h in argon atmosphere. Fig. 2a–d shows the resultant XRD patterns after the 500 °C, "argon" annealing.

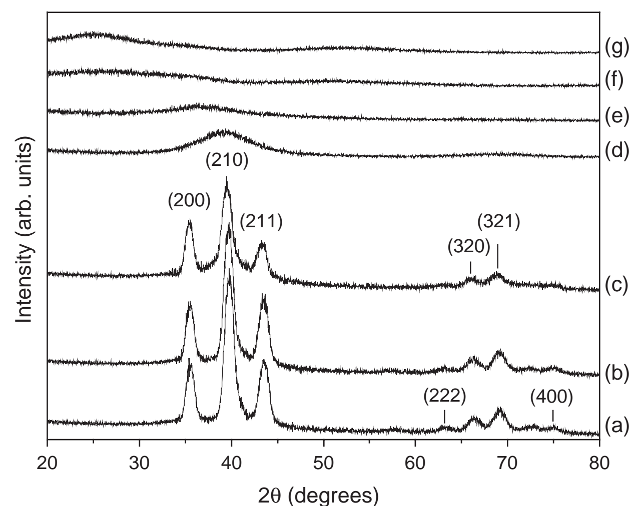

Fig. 1. A typical series of XRD patterns for W–O thin films deposited over a wide range of $P_{O/Ar}$ from (a) 1×10^{-3}, (b) 1×10^{-2}, (c) 0.1, (d) 0.2, (e) 0.4, (f) 0.6 (and 0.8 and 1), and (g) 2 (and 3).

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