Technology of metal oxide thin film deposition with interruptions

V. Khatko [a,*], J. Calderer [b], S. Vallejos [a], E. Llobet [a], X. Correig [a]

[a] Departament d'Enginyeria Electronica, Universitat Rovira i Virgili, Campus Sescelades 43007 Tarragona, Spain

[b] Universitat Politecnica de Catalunya, Departament d'Enginyeria Electronica, Campus Nord 08034 Barcelona, Spain

Abstract

The idea to obtain metal-oxide films with small grain size is to use a special regime of thin film deposition by r.f. sputtering of pure metal or metal oxide targets. This regime includes the deposition of thin films with one or several interruptions during the deposition process. WO_3 films were r.f. sputtered onto pure and oxidized silicon wafers. Four types of films were prepared, i.e. using continual deposition, one, two and three interrupted depositions with an actual deposition time of 40 min. The interruption time changed from 0.5 min to 5.0 min for the different samples. It was found that the total thickness of WO_3 films decreased with the increase of the number of interruptions and the increase in interruption time. Phase composition and features of surface morphology of the films deposited and annealed in the temperature range from room temperature to 900 °C have been investigated by XRD and AFM, respectively. It is shown that grain size in the metal oxide films decreased essentially with the increase of the number of interruption during the deposition process.

Keywords: R.f. sputtering; Deposition with interruptions; Tungsten trioxide thin films properties

1. Introduction

Tungsten trioxide (WO_3)has interesting physical and chemical properties, which make it useful for a wide spectrum of technological applications. For example, tungsten trioxide is an important material for electrochromic [1] and photoelectrochemical devices [2], catalysts [3] and gas sensors [4,5]. Nowadays, WO_3-based films are considered as one of the most interesting materials for detecting nitrogen oxides and other species such as NH_3, CH_4 and CO [4-9]. Reducing the grain size of active layers is one of the key factors to enhance the gas sensing properties of semiconductor metal oxide sensors [10,11].

The idea to create metal-oxide films with small grain size consists of using a special regime of thin film deposition by the dc magnetron, ion-beam or r.f. sputtering of pure metal or metal oxide targets. This regime includes the deposition of thin films with one or several interruptions of the deposition process [12,13].

----

* Corresponding author. Tel.: +34 977558653; fax: +34 977559605. E-mail address: vkhatko@urv.cat (V. Khatko).

Early systematic investigations of the growth kinetics of pure metals evaporated on amorphous carbon substrates have revealed that, after interrupting a continuous vapour deposition period by closing the beam shutter, the metal particles continued to grow for up to several minutes with decreasing speed [14-16]. At constant temperature, after re-opening the shutter, particle growth resumed with a delay being similar to that of particle nucleation. It was shown that there are at least two different mechanisms of adatom diffusion. There exist at least two binding states for the metal atoms with energies of about 1 eV for regular states and in the range from 1.5 to 1.7 eV with abundance of 10^{13} to 10^{14} cm^{-2} [14,16]. The occurrence of growth transients after closing the beam shutter requires re-emission of adatoms from the sites with higher energy in an activated process of particle growth. Porosities in the substrate surface could be responsible for temporarily trapping of adatoms in states with higher energy.

The detailed evolution of stress in thin films that grow by the Volmer–Weber (VW) mechanism during ultra-high vacuum deposition and growth interrupts was explored using real-time wafer curvature measurements [17–19]. It was shown that reversible stress changes during the interruption of thin film

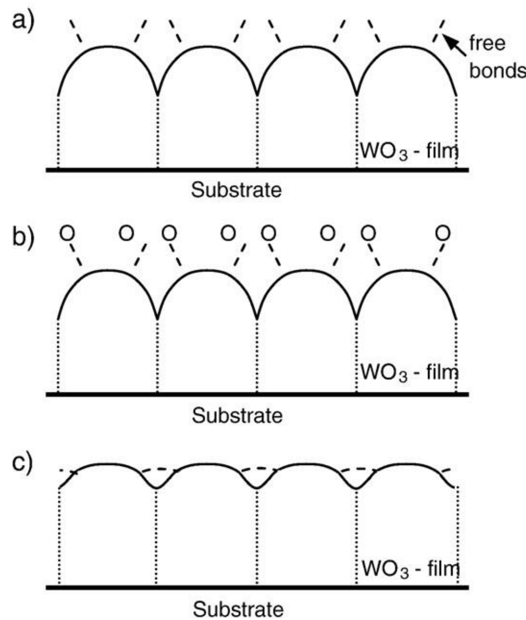

Fig. 1. Schematic illustrations of the manner of a film growth (a) and an equilibrium surface formation during interruption processes (b,c). Subplots b and c show the saturation of surface free bonds by oxygen atoms (b) and the structural relaxation of the surface (c).

growth are phenomenologically similar in the pre-coalescence and post-coalescence growth regimes. It was suggested that the reversible stress changes are associated with changes in the concentration of atomic defects on the substrate and film surface [19]. At the pre-coalescence stages of growth initiation, the dominant defects are isolated adatoms. At the post-coalescence stages, film surface is likely to be atomically rough, with excess adatoms, ledges and other defects. When film grow this interrupted, the defect population decays to the equilibrium value as excess adatoms diffuse to incorporation sites and excess defects are eliminated [19].

During the interruption of the deposition process at the postcoalescence stages of film growth, an equilibrium film surface can be formed due to the free surface bond saturation by the atoms from the residual atmosphere and/or the structural relaxation of the interface. Fig. 1 illustrates, for the two possible cases, the way in which the equilibrium surface is formed during an interruption process.

The saturation of metal films by oxygen atoms from the residual atmosphere has been shown earlier by the investigation of sputtering-deposited molybdenum films [20]. It could be realized by the formation of bonds between metal atoms and O^-ions accelerated from the target (Fig. 1b). It is known that a deposited thin film tries to minimize its total energy by keeping its surface area as small as possible to obtain an ideally flat surface. Surface diffusion of the adatoms makes possible the occupancy of empty sites in the film lattice and can lead to less surface area by filling in the valleys and leveling the atom peaks to give a lower surface energy
[19,21,22] (Fig. 1,c).

Thus, the surface diffusion of adatoms during interruption of the deposition could promote both film growth continuation [14-16] and structure relaxation of the film surface [19,21,22]. For the subsequent prolongation of the deposition process, film growth begins over again on the new "extra" equilibrium surface (relaxed surface) and the average grain size of the film at the surface could be smaller than in the original film. The equilibrium surface is sufficiently rough and there can be coalescence between both new islands and a new island and an existing film grain [22]. Fig. 2 shows a qualitative representation of the influence of the deposition interruptions on thin film thickness and grain size growth. The qualitative views of the dependencies of film thickness and grain size on deposition time were built on the base of theoretical and experimental data presented in Ref. [21]. So, Fig. 2,a sketches out the change in film thickness after each interruption. Lines 0, 1 and 2 present the change in film thickness as a function of deposition time for the film deposited without interruptions (line 0) and with one (line 1) and two (line 2) interruptions, respectively. Lines 1 and 2 show the time delay necessary for the nucleation of new particles [14]. The points 0, 1 and 2 define the film thickness after the end of the deposition process. Fig. 2,b shows a reiteration of the nucleation of grains on each new "extra" equilibrium surface formed after the interruption of the deposition process. Lines 0′, 1′ and 2′ present grain growth in the film as a function of deposition time for the film deposited without interruption (line 0′) and with one (line 1′) and two (line 2′) interruptions, respectively. The points 0′, 1′ and 2′ define grain size in the films after the end of the deposition process. The differences in grain size after the first and second interruption are related to the coalescence between both new islands and a new island and an existing grain in the film [14,22].

In previous studies it has been shown that using a deposition process with interruptions leads to WO_3 films with a decreased average grain size and better sensitivity to toxic gases[12,13].The aim of this paper is to study the influences of interrupting the deposition process and interruption time on the changes in film thickness, chemical composition, structure and surface morphology of WO_3 thin films.

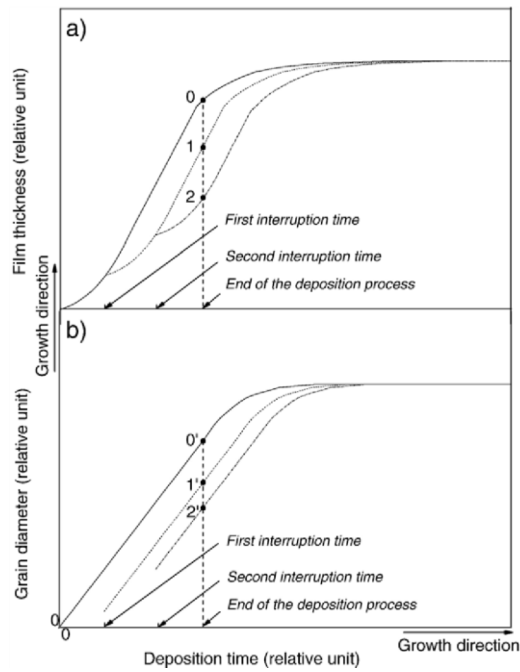

Fig. 2. Qualitative views of the dependencies of film thickness (a) and grain size (b) on deposition time. Labels 0, 1 and 2 correspond to deposition processes without and with one and two interruptions, respectively.

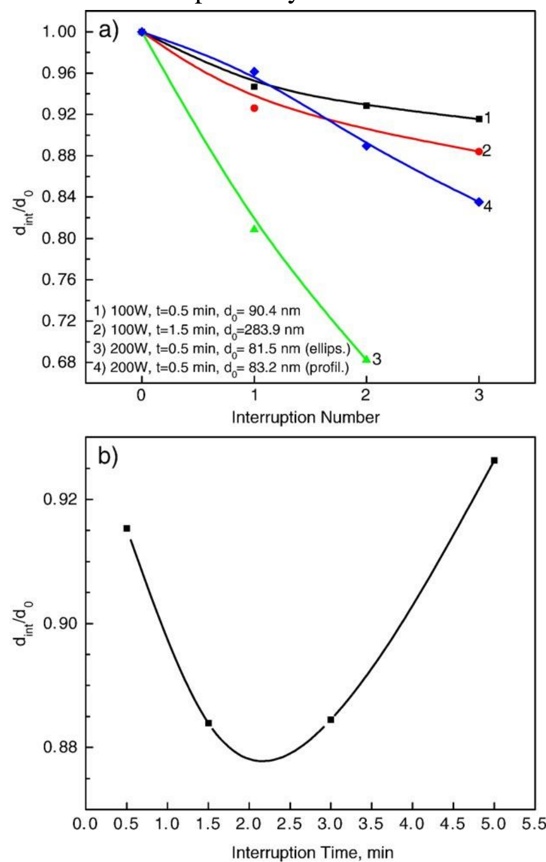

Fig. 3. Relative change of the metal oxide film thickness (d_{int}/d_0) as a function of the number of interruptions (a) and interruption time (b). For reference, the experimental data obtained at the sputtering power of 200 W [Ref. [13]] are presented as well.

2. Experimental

Tungsten oxide films were deposited onto boron-doped (110 Ω cm) Si(100) wafers by reactive r.f. magnetron sputtering using an ESM100 Edwards sputtering system. A metal target of 99.95% purity with a diameter of 100 mm and thickness of 3.175 mm was used. The target to substrate distance was set to 70 mm [13]. One part of the silicon wafers used was oxidized in dry oxygen at 1100 °C. The thickness of the SiO_2 films was about 150 nm. All wafers were held in thermal contact with a holder during the deposition process. The substrate temperature was kept constant during film deposition at room temperature. The base pressure in the sputtering chamber was 6×10^{-3} mbar.
The sputtering atmosphere consisted of Ar–O_2 mixed gas and its flow rate was controlled by separate gas flow-meters to provide an Ar:O_2 flow ratio of 1:1. The pressure in the deposition chamber during sputtering was 5×10^{-3} mbar. The r.f. sputtering power was 100 W.

Four types of tungsten oxide films were prepared. For the first type a non-interrupted sputtering process was used. In the deposition of films type 2, 3 and 4, the sputtering process was interrupted once, two and three times, respectively. A shutter was used to interrupt the deposition process. As a rule, the actual deposition time without interruption was 40 min. Nevertheless, for several tungsten oxide films deposited with interruptions, the deposition time was up to 2 h. The interruption time changed from 0.5 min to 5.0 min for the different samples. The film thickness and refractive index were measured by ellipsometry (PLASMOS 2000) at 50° and 60° of incidence angle. As-deposited and annealed tungsten oxide films had refractive index of 2.08–2.13 that corresponded to those obtained in Ref.[23].

X-ray diffraction (XRD) measurements were made using a Siemens D5000 diffractometer (Bragg–Brentano parafocusing geometry and vertical θ–θ goniometer) fitted with a curved graphite diffracted-beam monochromator and Soller slit, 0.2 mm receiving slit and scintillation counter as detector. The angular range was between 19° and 70° for 2θ. Data were collected with an angular step of 0.02° and 6 s per step and sample rotation. CuKα radiation was obtained from a Cu X-ray tube operated at 40 kV and 30 mA. To run XRD measurements at high temperature, an Anton-Paar HTK10 temperature chamber was attached to the diffractometer. Temperature patterns were collected at $\Delta T=100$ °C. The time for X-ray pattern recording was up to 60 min at each definite temperature. A static airatmosphere was used throughout the measurements.

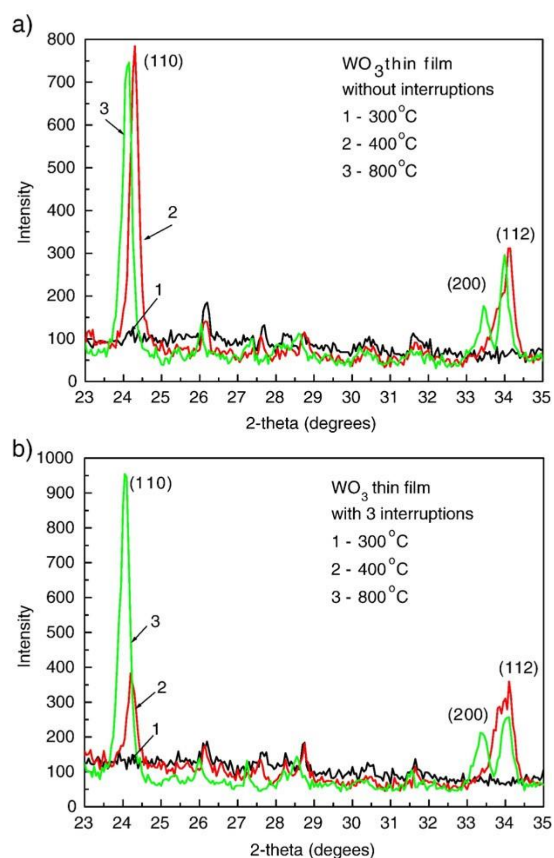

Fig. 4. X-ray diffractograms of WO_3 thin films deposited without (a) and with three interruptions (b). 1, 2 and 3 correspond to the temperature of the XRD measurement.

As-deposited tungsten oxide films were studied by Auger spectrometry to investigate oxygen segregation on the equilibrium surface built up during deposition interruption. The tungsten oxide layer surface and the chemical element distribution in the samples were examined with a PHI-660 Auger spectrometer operating at 3 kV and using a probe diameter up to 1 μm. Auger electron collection depth was up to 2.0 nm. The layer thickness removed during each step of argon ion etching was up to 0.9–1.0 nm. The morphology of the WO_3 thin films was determined by Atomic Force Microscopy (AFM) from Molecular Imaging (PicoScan controller) in tapping mode. The estimation of grain size and image processing were achieved using MetaMorph 6.1 and WSxM 4.0 software respectively. The mean diameter of grains was calculated for a population of one hundred elements. The standard error of the mean diameter of grains (SEM) was calculated with the following expression: SEM= SD/square root (*n*), where SD is the standard deviation and *n* the number of elements. The standard error of the mean diameter of grains was between ±0.14-±0.52 nm in each case.

without interruptions

with three interruptions(t= 0.5 min)

a) b) c)

Fig. 5. AFM surface morphology and roughness profile of WO_3 thin films without interruptions and with three interruptions. (a) as deposited, (b) annealed at 400 °C and (c) annealed at 450 °C.

3. Results and discussion

3.1. Measurement of film thickness

Fig. 3 shows the relative change of the metal oxide film thickness (d_{int}/d_0) as a function of the number of interruptions (Fig. 3,a) and interruption time (Fig. 3,b). Here, d_{int} and d_0 are the thickness of WO_3 thin films deposited with a definite number of interruptions (int=0, …,3) and without interruptions (int=0), respectively. For comparison, the experimental data obtained at the r.f. sputtering power of 200 W taken from Ref. [13] is presented in Fig. 3,a as well.

It can be seen that the total thickness (d_{int}) of WO_3 thin films deposited with interruptions decreases when the number of interruptions during the deposition process increases (Fig. 3,a). This result is verified for the different total thickness of WO_3 thin films and the different r.f. sputtering power of the deposition process. The relative change in the metal oxide film thickness decreases when the total thickness of WO_3 thin films and r.f. sputtering power are increased. In the latter case, using higher sputtering power (200 W) has an extremely strong influence on the properties and total thickness of the WO_3 thin films [13]. There is a difference in the thickness measured by profilometry and ellipsometry for the tungsten oxide thin films deposited with interruptions during the deposition process. For examples, the relative changes in the thickness of the films deposited with two interruptions have values of 0.89 and 0.68 measured by profilometry and ellipsometry, respectively (Fig. 3,a). This result shows that “extra” interfaces are introduced into the body of a thin film during each interruption of the deposition process. At this point we can conclude that the features of the surface relaxation process influence on the formation of “extra” interfaces.

This is confirmed by a stress relaxation study [17–19] and the experimental data presented in Fig. 3, b. It can be seen that the duration of interruption influences on the total thickness and the relative change of the metal oxide film thickness. For explaining this functional dependence we will use the experimental data obtained in [14,15] and presented above. It can be assumed that there is some relation between the time in which a film continues to grow after the shutter has beenclosed and the time delay for the film to resume its growth after re-opening the shutter. Increasing the time in which the film continues to grow could decrease the time delay before resuming its growth. In this case, the relative change of the metal oxide film thickness can have a minimum at a definite value of the interruption time, just as Fig. 3,b shows. We can conclude that the process of film surface relaxation has a definite time (the time for the connection of all free bonds).

3.2. Structure of the WO_3 films

Fig. 4 shows the X-ray diffractograms of WO_3 thin films deposited onto a silicon substrate from $2\theta=23.0°$ to 35°. XRD data showed that the structure of as deposited WO_3 films is amorphous. After annealing at 400 °C one monoclinic phase is present in the thin film that is described with the space groups Pc (ICDD card no. 87-2386, cell parameters: a=5.277 Å, b=5.156 Å, c=7.666 Å, β=91.742°). XRD patterns contain (110),(200) and (112)reflections from the monoclinic phase (Pc).

It can be seen that the process of thin film crystallization has a different activity for the different types of WO_3 thin films. The crystallization in the thin film prepared with three interruptions during its deposition (Fig. 4b) is slower than in films prepared without interruptions (Fig. 4a). This can be derived by comparing the intensities of (110) peaks and their full widths at half maximum. WO_3 thin films prepared without interruptions have maximum intensity of (110) peak and full width at half maximum of this peak is minimal. It is worth noting that the low-temperature monoclinic phase in WO_3 thin films was stable in a temperature range from 400°C to 800°C. WO_3 thin films were

sublimated at 900°C. The same result was obtained for WO_3 thin films deposited onto oxidized silicon wafers.

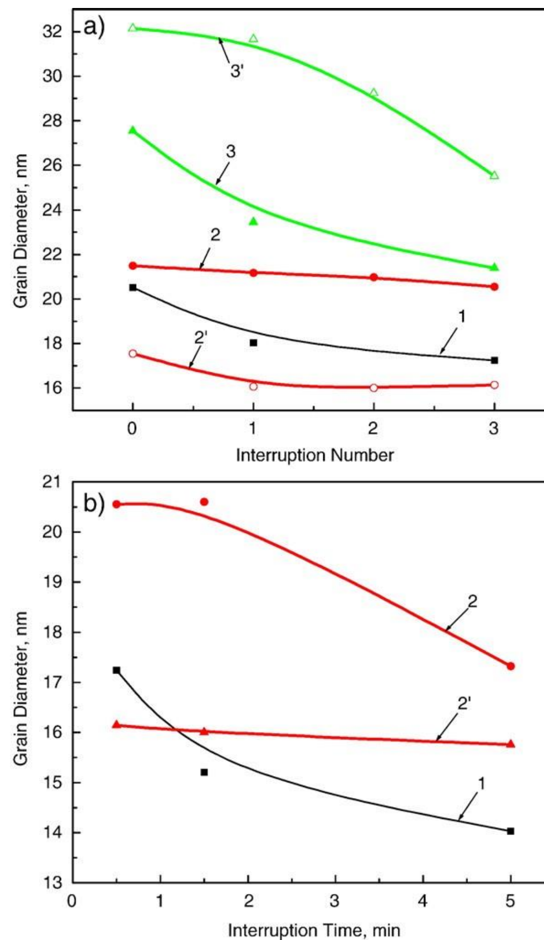

Fig. 6. Mean diameter of grains in WO_3 films as a function of the number of interruptions (a) and interruption time (b). 1, 2 and 3 are labels for Si–SiO_2– WO_3 structures as-deposited and annealed at 400 °C and 450 °C, respectively. 2′ and 3′ are labels for Si–WO_3 structures annealed at 400 °C and 450 °C, respectively.

The fact that the monoclinic phase with Pc symmetry exists in WO_3 thin film deserves some comments. The existence of low-temperature Pc phases has been reported in gas-evaporated WO_3 microcrystals analyzed by Raman spectroscopy [24,25]. The reason for the existence of Pc phase in these microcrystals could be either high compression stresses or surface effects on the grains or interfaces [26]. In our case the basic reason for the existence of a Pc phase in WO_3 thin films could be compressive stresses into the layers.

3.3. Morphology of the WO_3 films

In this section we tried to find a confirmation that the “extra” interfaces influence on the morphology, roughness and mean grain size formed in WO_3 surface layers during thin film growth. We analyzed Si–SiO_2–WO_3 structures as deposited and annealed at 400 °C and 450 °C since these structure are used very intensively in the preparation of gas sensors [4,5,12,13]. The results obtained were compared with the experimental data for Si–WO_3 structures annealed at 400 °C.

Fig. 5 shows the surface morphology and roughness profiles of the WO_3 films as deposited and annealed. It can be seen that tungsten oxide grains in the films deposited without interruptions try to reach an ordered distribution after annealing. That is not so clear for all of the films with three interruptions. The occurrence of an ordered distribution is correlated to the results obtained by XRD. The crystalline structure in the films prepared with three interruptions is not fully ordered as in the films prepared without interruptions. On the other hand, the roughness profile analysis along the horizontal lines of the AFM pictures shows that the samples deposited with three interruptions are smoother than the ones deposited without interruptions.

Fig. 6 shows the mean diameter of grains in WO_3 films as a function of the number of interruptions and their duration. It can be seen that grain diameter decreases from 20.5 nm down to 17.0 nm in as deposited $Si–SiO_2–WO_3$ structures without and with 3 interruptions respectively. Increasing the interruption time from 30 s up to 5 min results in a further reduction of grain size from 17.0 nm down to 14.0 nm. When annealing at 400 °C, the process of WO_3 film crystallization results in a slight increase in the diameter of the grains. There is a tendency showing that the higher the number of interruptions is, the lower the increase in grain size during the annealing process is.

3.4. Discussion

On the base of the experimental results obtained we can summarize that the introduction of the "extra" interfaces during the deposition interruptions influences the process of WO_3 film crystallization retarding it.

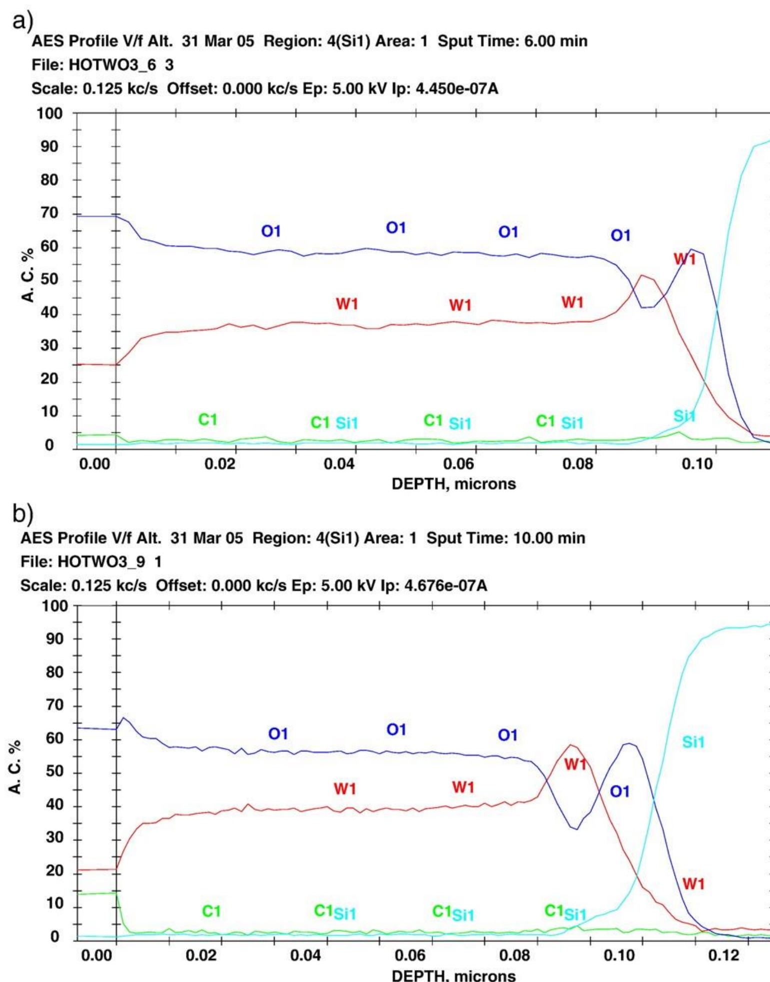

Fig. 7. Auger profiles of chemical elements into WO_3 thin films prepared without (a) and with three interruptions (b) during the deposition process. A.C. stands for atomic concentration in %.

Fig.7shows Auger profiles for twotypesofas-depositedWO_3 thin films on silicon wafers. It can be seen that the chemical element composition on the surface of tungsten oxide film corresponds to stoichiometric WO_3. The change in the ratio of tungsten to oxygen atoms observed after argon ion etching of the film surface is due to the difference in the scattering coefficient of oxygen and tungsten [27]. The existence of a narrow area (up to 20 nm) close to the film-substrate interface containing a high amount of tungsten atoms could be explained by the formation of WO_{3-x} (Magneli phases) [28]. Nevertheless WO_{3-x} phases were not detected by the XRD method.

The basic conclusion from Fig. 7 is that there is no heterogeneity at the profiles of tungsten and oxygen atoms. The absence of any segregation of oxygen or tungsten atoms into the thin film body evidences that the process of free bond saturation by the atoms from residual atmosphere on the "extra" interface is not clearly realized or cannot be detected by Auger spectroscopy. This result is similar the one presented in Ref. [17] where oxide layers were not observed in Al films deposited with two interruptions. The tendency to obtain smoother surfaces in WO_3 films deposited with several interruptions shows that the process of minimization of film surface energy was repeated several times during interruptions. It could be suggested that the "extra" interface is formed due to the structural relaxation of the additional interface during the interruption time.

4. Conclusions

The properties and structural features of WO_3 thin film layers deposited with interruptions have been studied by XRD, Auger spectroscopy and AFM. The WO_3 films were deposited by r.f. sputtering onto pure and oxidized silicon wafers at an argon/ oxygen flow ratio of 50/50, r.f. power of 100 W and a total pressure of 5×10^{-3} mbar. Four types of films were prepared, i.e. using continual deposition, one, two and three interrupted depositions with an actual deposition time of 40 min. The total thickness of WO_3 thin films deposited with interruptions decreases when the number of interruptions during the deposition process increases. All as-deposited WO_3 films have an amorphous structure. After annealing at 400 °C, a low-temperature monoclinic phase with Pc symmetry is present in the films. This phase was very stable up to 800 °C and the interruption of deposition influenced on WO_3 film crystallization by retarding it. On the base of the experimental data obtained and the references analyzed it could be suggested that the "extra" interface is formed intothebodyofthefilmduetosurfacestructuralrelaxationduring its interrupted growth. At the same time, the experimental data obtained by Auger spectroscopy did not show any segregation of oxygen or tungsten atoms into the WO_3 film body.

References

[1] G.G. Granqvist, Sol. Energy Mater. Sol. Cells 60 (2000) 201.

[2] A. Di Paola, L. Palmisano, A.M. Venezia, V. Augugliano, J. Phys. Chem. B103 (1999) 8236.

[3] A. Löfbeg, A. Frennet, G. Leclercq, L. Leclercq, J.M. Giraudon, J. Catal. 189 (2000) 170.

[4] P. Shaver, Appl. Phys. Lett. 11 (1967) 255.

[5] D.G. Dwyer, Sens. Actuators, B, Chem. 5 (1991) 155.

[6] A.A. Tomchenko, V.V. Khatko, I.L. Emelianov, Sens. Actuators, B, Chem. 46 (1998) 8.

[7] A.A. Tomchenko, I.L. Emelianov, V.V. Khatko, Sens. Actuators, B, Chem. 57 (1999) 166.

[8] Y.K. Chung, M.H. Kim, W.S. Um, H.S. Lee, J.K. Song, S.C. Choi, K.M. Yi, M.J. Lee, K.W. Chung, Sens. Actuators, B, Chem. 60 (1999) 49.

[9] D.S. Lee, S.D. Han, J.S. Huh, D.D. Lee, Sens. Actuators, B, Chem. 60 (1999) 57.

[10] I. Jimenez, J. Arbiol, G. Dezanneau, A. Cornet, J.R. Morante, Sens. Actuators, B, Chem. 93 (2003) 343.

[11] S.-H. Wang, T.-C. Chou, C.-C. Liu, Sens. Actuators, B, Chem. 94 (2003) 475.

[12] V. Khatko, J. Calderer, E. Llobet, X. Correig, Proceedings of the European Materials Conference E-MRS 2004 FALL MEETING, Warsaw (Poland), Sept. 6–10 2004, p. 36.

[13] V. Khatko, J. Calderer, E. Llobet, X. Correig, Sens. Actuators, B, Chem. 109 (2005) 128.

[14] A.A. Schmidt, R. Anton, Surf. Sci. 322 (1995) 307.

[15] A.A. Schmidt, H. Eggers, K. Herwig, R. Anton, Surf. Sci. 349 (1996) 301. [16] R. Anton, A.A. Schmidt, Surf. Sci. 357-358 (1996) 835.

[17] J.A. Foro, S.J. Hearne, J.A. Hunter, P. Kotula, E. Chason, S.C. Seel, C.V. Thompson, J. Appl. Phys. 89 (2001) 4886.

[18] C. Friesen, C.V. Thompson, Phys. Rev. Lett. 89 (2002) 126103.

[19] C. Friesen, S.C. Seel, C.V. Thompson, J. Appl. Phys. 95 (2004) 1011.

[20] T.T. Bardin, J.C. Pronko, R.C. Budhan, et al., Thin Solid Films 165 (1988) 243.

[21] C.A. Neugebauer, in: L.I. Maissel, R. Glang (Eds.), Condensation, nucleation, and growth of thin films, Handbook of thin film technology Chapter 8, McGraw-Hill, N.Y., 1983.

[22] F. Spaepen, Acta Mater. 48 (2000) 31.

[23] D.J. Taylor, J.P. Cronin, L.F. Allard Jr, D.P. Birnie III, Chem. Mater. 8 (1996) 1396.

[24] M. Arai, S. Hayashi, K. Yamamoto, S.S. Kim, Solid State Commun. 75 (1990) 613.

[25] S. Hayashi, H. Sugano, H. Arai, K. Yamamoto, J. Phys. Soc. Jpn. 61 (1992) 916.

[26] A.G. Souza Filho, P.T.C. Freire, O. Pilla, A.P. Ayala, J. Mendes Filho, F.E.A. Melo, V.N. Freire, V. Lemos, Phys. Rev. 62 (2000) 3699.

[27] D. Briggs, M.P. Seach (Eds.), Practical surface analysis by Auger and X-ray photoelectron spectroscopy, MIR, Moscow, 1987, 600 pp. (in Russian).

[28] A. Al Mohammad, M. Gillet, Thin Solid Fims 408 (2002) 302.