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Improvement of oxidation and corrosion resistance of Mo thin films by alloying with Ta

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ABSTRACT

Molybdenum thin films are commonly used as electrode materials for thin film transistor liquid crystal displays. As low-temperature oxidation deteriorates their electrical resistivity, the aim of this study was to improve their oxidation resistance by alloying with tantalum. Thin films with tantalum contents ranging from 0 to 100 at.% have been synthesized by magnetron co-sputtering. Beside the evaluation of microstructure and resistivity with increasing tantalum content, special emphasis is laid on formation of surface oxides during exposure to elevated temperature and humidity. The formation of a transparent tantalum oxide minimizes surface oxidation, preventing growth of intensively colored molybdenum oxide scales. Potentio-dynamic measurements further highlight the positive influence of tantalum, evidencing the development of a passive region and a drop of the corrosion current density to almost zero.

1. Introduction

For thin film transistor liquid crystal displays (TFT-LCD), molybdenum (Mo) films are frequently used as conducting materials for gate and source/drain electrodes as well as bottom and capping layers for metallization [1,2]. Mo is the main choice for these applications because of its relatively low electrical resistivity, low coefficient of thermal expansion resulting in its good adhesion to glass substrates, thermal stability, its diffusion barrier abilities, and easy chemical pattering [3,4]. However, Mo is known to readily oxidize even at room temperature, which has stimulated scientific attempts to understand its electrochemical behavior and to minimize corrosion [5–7]. A decline of corrosion may be achieved by suitable surface treatments or conditions, but commonly it is minimized by alloying [8]. The choice of an appropriate alloying element is crucial as the properties mentioned may deteriorate.

In a recent work on the suitability of different alloying elements [5], the elements Ta, Nb, and Cr have been identified as potential candidates to improve the oxidation and corrosion properties of Mo thin films. In particular, alloying 37.7 and 39.5 at.% of Ta to sputtered Mo films results in the formation of a body-centered cubic (bcc) Mo–Ta solid solution [9]. This solid solution has been reported to yield an improved thermal stability of the low work function required for complementary metal oxide semiconductor applications, compared to unalloyed Mo films [10]. Despite these reports, a comprehensive study of the effect of the Ta content on microstructure, corrosion, and oxidation resistance of sputtered Mo–Ta films over a wide composition range is missing. Thus, this study focuses on the influence of Ta alloying on Mo thin films regarding microstructure, electrical resistivity, surface oxidation, and electrochemical behavior. Its main emphasis is on the resulting effects on surface oxidation after exposure in a climatic chamber, evidencing by X-ray photoelectron spectroscopy (XPS) the preferred oxidation of Ta compared to Mo and the formation of a transparent Ta oxide scale. Furthermore, electrochemical measurements address the corrosion behavior of the films and show again the positive influence even for small Ta fractions.

2. Experimental details

The films investigated within this work were deposited by co-sputtering from Mo and Ta targets with dimensions of Ø 50.8 × 6 mm and purities of 99.97% and 99.95%, respectively, in a laboratory-scale unbalanced dc magnetron sputter system on soda lime glass (Corning EAGLE2000TM AMLCD, size 50 × 50 mm^2). Prior to deposition, the substrates were ultrasonically cleaned in a commercial detergent from Borer Chemie AG and, after mounting to the substrate holder, ion etched for 5 min at −500 V. Simultaneously, the targets were sputter pre-cleaned for 2 min against a shutter using a magnetron current of 0.1 A.

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For both ion etching and target cleaning, an Ar flow of 100 sccm resulting in a pressure (p) of 0.55 Pa was used. For thin film deposition, the Ar flow was set to 30 sccm ($p = 0.35$ Pa), a bias voltage of −50 V was applied and the substrates were heated to 120 °C. The magnetron currents of both targets were varied from 0 to 0.35 A (corresponding to power densities up to 6.9 W/cm^2) to deposit films ranging in their composition from pure Mo to pure Ta (see Table 1). The deposition times were adjusted so that a film thickness of ~200 nm was obtained for all films. The film thickness was confirmed by cross-sections of broken samples for each composition using a scanning electron microscope (SEM, Zeiss EVO 50). The chemical composition of the films was characterized by energy-dispersive X-ray spectroscopy (EDX) using an Oxford Instruments INCA extension to the SEM (Table 1).

The crystallographic structure was investigated using a Bruker-AXS D8 Advance X-ray diffractometer (XRD) in Bragg–Brentano geometry with Cu Kα radiation. The size of the coherently diffracting domains was determined by applying a pseudo-Voigt function to the diffraction peaks [11]. The electrical sheet resistivity of the films was measured with a Jandel RM2 four-point probe.

Climatic chamber exposure tests were performed at a relative humidity of 85% at 85 °C for 168 h (i.e., for 1 week). Before and after exposure, each sample was weighed to determine the specific mass change using a precision balance with a resolution of 0.01 mg, while the change of surface coloration was assessed by optical inspection afterwards. Further insight into the oxidation states of selected films was gained by applying XPS, using an Omicron Nanotechnology Multiprobe surface analysis system with a DAR 400 X-ray source, an XM 500 quartz crystal monochromator (X-ray excitation energy of 1486.7 eV, Al Kα_1), and an EA 125 hemispherical electron energy analyzer with a 5 channel pulse counting channeltron. The overall energy resolution of the whole system is 0.4 eV at a pass energy of 10 eV. The binding energy was corrected by using the C—C bond of the C 1 s peak of residual hydrocarbon surface contaminants at 284.6 eV as reference. Measurements were performed sequentially on each sample in the as-received state, after heating to 350 °C for 20 min to remove volatile surface contaminations, and after Ar$^+$ sputtering at 2 keV for 20 min, without breaking the vacuum to avoid re-contamination. The obtained spectra were fitted using a convolution of a Lorentzian and a Gaussian profile (Voigt function) [12].

Potentio-dynamic measurements to determine polarization curves were performed with a GAMRY potentiostat to characterize the corrosion behavior of the films. Each sample was immersed into 0.9% NaCl aerated aqueous solution at room temperature. As a counter electrode, a platinum plate was used, which was recrystallization-annealed prior to each measurement. A saturated calomel electrode (SCE) was applied as the reference electrode having a potential of 241 mV$_{SHE}$ (standard hydrogen electrode). In this work, all potentials are reported with respect to SCE. Before the actual measurement, the open circuit potential (OCP) was determined for 1 h (to reach equilibrium) and the starting potential was 100 mV lower than the OCP. The scan rate was set to 600 mV/h from the starting potential (i.e., OCP −100 mV) up to 1.2 V. The Tafel plot was applied to each measured curve at the free corrosion potential to determine the corrosion current density i_{corr}.

Table 1
Magnetron currents applied to the Mo and the Ta targets as well as respective Ta content of the films deposited.

Magnetron current [A]		Ta content [at.%]
Ta target	Mo target	
0	0.35	0
0.05	0.35	8.4
0.1	0.35	18.9
0.2	0.35	32.3
0.35	0.35	48.7
0.35	0.2	63.7
0.35	0	100.0

3. Results and discussion

3.1. Chemical composition and microstructure

All films deposited have a bright shiny metallic surface and show a mirror-like refection. Furthermore, they adhere to the glass substrates without any evidence of delamination. In order to obtain information about the crystal structure, XRD measurements in Bragg–Brentano geometry were performed. In Fig. 1, the diffractograms of selected films are shown and the standard peak positions of bcc–Mo, bcc–Ta, and tetragonal Ta are indicated as dashed lines [13,14]. All films which contain Mo show a bcc structure and a peak shift from the Mo peak positions toward Ta can be observed with increasing Ta content. No discrete phase forms, which is in good agreement with literature as the binary system Mo–Ta forms a solid solution in equilibrium [15]. Moreover, as the lattice parameter of the bcc–Ta cell is larger ($a = 3.3029$ Å) than for bcc–Mo ($a = 3.1470$ Å), the shift toward lower angles with increasing Ta content according to Bragg's law is compulsory [16].

Under the applied deposition conditions with low energy ion bombardment using a substrate bias voltage of −50 V and a low substrate temperature of 120 °C, the metastable β-Ta phase is formed in the pure Ta film. While in the past, numerous crystal structures have been suggested for this phase, researchers seem to agree on a tetragonal unit cell for β-Ta, despite the reported varying lattice parameters (see e.g. [17] for a summary of reported structures for β-Ta). The peaks of tetragonal Ta are reported by Jiang et al. to occur at $2\Theta = 33.64$ and 70.55°, referred to as (002) and the (004) reflections, whereas Zhang et al. observed two peaks at $2\Theta = 33.8$ and 70.9°, respectively [18,19]. This corresponds well to the position of the (002) peak, given at 33.692° in ref. [20]. β-Ta has been reported to form under non-equilibrium film growth conditions, i.e. without or with insufficient assistance of substrate heating [21]. The β-Ta peaks observed in Fig. 1 lie well between the 2Θ values of 33.64 and 33.8° for the (002) and 70.55 and 70.9° for the (004) orientation, as reported by Jiang et al. and Zhang et al., respectively [18,19]. To obtain a pure Ta film in the stable bcc structure (i.e., α-Ta), increased substrate temperatures, a substrate not prone to form oxides on the surface, or higher film thickness would be required, respectively [22,23]. It is also possible to transform the β- to the α-Ta by annealing at temperatures of ~700 °C [24].

The size of the coherently diffracting (110) domains was determined by applying a pseudo-Voigt function to the diffraction peaks shown in Fig. 1. Determined from the (110) peak, the pure Mo film has a domain size of ~33 nm, which is slightly increasing up to ~38 nm for the film with 8.4 at.% Ta and then reaching a plateau at ~28 nm for films with 32.3 at.% Ta and higher. The slight decrease in the domain size for comparable Mo and Ta contents can be attributed to the formation of a solid solution with hindered ad-atom diffusion during film growth. The pure Ta film has an estimated coherently diffracting domain size, determined for the (004) peak the β-phase, of ~28 nm. While the domain size is

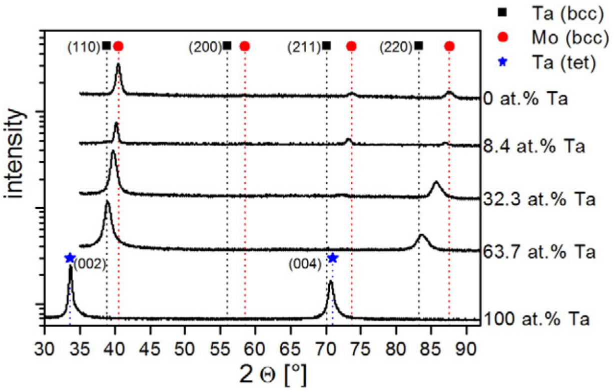

Fig. 1. XRD diffractograms of Mo–Ta films with varying Ta contents.