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ScienceDirect
Scripta Materialia 105 (2015) 18–21
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Anodization of sputtered metallic films: The microstructural connection

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Received 8 April 2015; accepted 19 April 2015
Available online 29 April 2015

A simple microstructural rationale for successful anodization of metallic films into ordered oxide nanostructures has been identified. It applies to three of the most commonly studied systems, Zr, Ti and Al films and can be extended to other such oxides. A dense Zone T or II microstructure, in sputtered films, is the most critical ingredient. While $T_{\text{substrate}} > 0.3T_{\text{melting}}$ is the simplest route, pressure and plasma heating can also be exploited. Such microstructures are also associated with a unique growth stress signature.

Keywords: Sputtering; Microstructure; Growth stress; Anodization

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The success of porous anodic alumina and titania in applications like templates [1] and solar cells [2] had sparked interest in anodized porous oxides. Anodized oxides of Zr [3,4], Hf [5], Nb [6,7], Sn [8] and W [9] were synthesized for their potential applications. For instance, these anodized oxides are still of interest as gas sensors [10–12]. In particular, zirconia is also appealing for solid oxide fuel cells [13] and tin oxide is a very promising candidate for Li-ion batteries [14].

While these have been synthesized predominantly as free standing membranes obtained by anodization of metallic foils; supported nanostructures, on a suitable substrate, would enhance the performance and range of applications. Anodization of metallic films obtained by sputtering is one common route for the synthesis of such supported nanostructures. While anodization conditions have been extensively studied, the role of microstructure of the starting metallic foil has been better understood only relatively recently [15–19]. Comparatively, in the case of films, fewer studies exist. In the ones that do, the film deposition conditions and structural parameters that yield nanostructures like foils [20,21], are arrived at empirically. If a rationale were available, laborious optimization of film deposition parameters could be avoided. In this work, one such simple microstructural rationale has been identified that greatly simplifies the optimization of film deposition parameters. Even though the substrate also plays a role, this manuscript deals only with the effect of the sputtering conditions. Though the work was done as part of a program for synthesizing nanoporous Zr oxide templates, it is found to be applicable to Al and Ti, the two most commonly studied systems, as well. The rationale should also work with any other metallic system.

It is shown that dense microstructures obtained under zone-T or zone-II sputtering conditions of Thornton's zone diagrams [22] yield anodized morphologies comparable to those obtained from foil anodization. Columnar films with voids under zone-I structure anodize to yield a "sponge-like" morphology. While the sputtered microstructure is affected by many variables, substrate temperature in excess of $0.3T_m$ (T_{melting} in K) of the metal is the simplest approach. Reduction in pressure or increasing the plasma power can also yield similar dense microstructure. These alternate parameters become particularly important if the films need to be deposited on substrates which cannot sustain elevated temperatures. In situ stress monitoring during sputtering shows that films which yield the required microstructure, whether by the $T > 0.3T_m$ criterion or any other combination of parameters, are all associated with a specific growth stress signature. A qualitative model developed explains the reasons for the difference in anodization behavior in films sputtered under different conditions. All the above; the zone based approach, the qualitative model and the stress signature are material system independent and therefore are universally applicable to any metallic system anodization.

The films were deposited on a rotating 2 cm square (1 0 0) Si substrate by dc magnetron sputtering of a 1 diameter target (Zr, 99.5% purity, ACI Alloys; Ti and Al, 99.7% purity, Kurt J. Lesker). An off-axis sputtering geometry with the target normal at 45° to the substrate normal was used. The substrates were degreased by sonication in

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http://dx.doi.org/10.1016/j.scriptamat.2015.04.017
1359-6462/

isopropanol and acetone, followed by rinsing in de-ionized water and drying in a nitrogen gas stream. Following a pump down to a base pressure of 10^{-7} Torr, the deposition was carried out at 5×10^{-3} Torr using purified 99.999% Ar. The base pressure and purification of the 99.999% Ar by a SAES getter were critical to obtaining metallic Ti and Zr films suitable for anodization. Zr films were deposited at target current of 75–150 mA (20–45 W) at 5 m Torr at substrate temperatures; 300, 500 and 700 °C. The target-substrate separation was maintained at 7.5 cm. Ti films were sputtered at target current of 125 mA (45 W) at separations of 4 cm and 9 cm at temperatures of 25 and 600 °C and at various pressures. Al films were deposited at a target current of 25 mA (10 W) at a target-substrate separation of 7.5 cm and at a pressure of 40 m Torr. The as deposited films were directly used for anodization. In situ growth stress evolution during the metal film deposition was studied by curvature measurements using a multiple beam optical stress sensor (MOSS) at near normal incidence [23].

Anodization of the thin films was done in a two electrode electrochemical cell with Pt wire as the cathode. Silver paint was used to make direct electrical contact to the sputtered films. Anodization of Zr, Ti and Al films was carried out in 0.35 M NH_4F dissolved in glycerol (20–60 V), 2 vol.% water and 0.02 M NH_4F (60 V) and 0.3 M oxalic acid (40 V) respectively. A high voltage (0–120 V) power supply unit (Aplab L1281) was used for the potentiostatic anodization experiments. After anodization, the samples were rinsed in de-ionized water and dried in a nitrogen gas stream. The film morphology was characterized by a scanning electron microscope (Zeiss FESEM, Ultra) at low accelerating voltages without any conductive coating. The substrate was cleaved to obtain the cross section.

The effect of varying substrate temperature during sputtering of Zr (10 nm/min) on film microstructure and its effect on anodization is summarized in Figure 1. Figure 1(a–d) clearly shows that with an increase in sputtering temperature from 25 to 700 °C, the sputtered metallic microstructure changes from a porous columnar structure to a dense one. The corresponding anodized morphology is seen to transition from a disordered spongy structure to a tubular one. For comparison, the tubular morphology from an anodized foil is shown in the inset in Figure S1. In contrast to the effect of varying temperature, the effect of varying the metal deposition rate for possible densification is shown in Figure S2. The effects, if any, are minimal.

For sputtered films, the effect of temperature is rationalized in terms of the *homologous temperature* ($T_{substrate}/T_{melting}$ *or* T_s/T_m) effect on surface and bulk diffusivities and its effect in turn on microstructure as shown in Thronton's model. At low pressures, like 5 m Torr, $T_s/T_m < 0.3$ results in amorphous to poorly crystalline columnar structures with voids (zone-I). This is due to the self-shadowing effect of the initial nuclei. The restricted adatom mobility does not fill up the voids between the initial nuclei. With an increase in temperature, $0.3 < T_s/T_m < 0.7$, higher surface diffusivity results in the voids being filled and hence, dense columnar structures (zone-T/zone-II) are formed. At even higher temperatures, $T_s/T_m > 0.7$ (zone-III), bulk diffusion results in an annealed recrystallized structure with equiaxed grains. The melting points of Zr and Ti are 2125 K and 1923 K respectively. Thus, $0.3T_m$ translates to 637 K or 364 °C for Zr. It can be seen from Figure 1 that Zr films sputtered at $700\ °C > 0.3T_m$, yield dense microstructures that in turn anodize to yield nanotubes. Those sputtered at lower temperatures yield porous columnar structures which anodize to yield spongy structures.

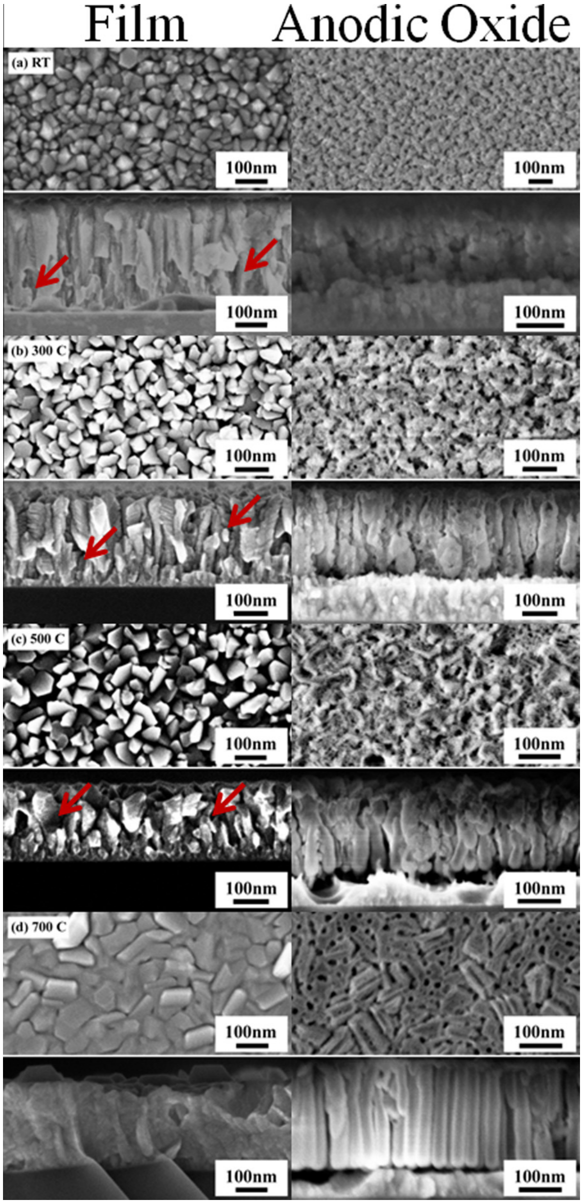

Figure 1. Variation in sputtered Zr film morphology, deposited at a rate of 10 nm/min, and the corresponding anodized morphology (60 V–1 min) with the substrate temperature (100 mA) at (a) room temperature (b) 300 °C, (c) 500 °C and (d) 700 °C. The upper and lower half in each image shows the top and the cross-sectional view respectively.

A similar effect of temperature on the anodization of Ti films has been observed previously [20,21]. The effect was rationalized in terms of the density of the films [20], but it was not investigated further. It was observed that films deposited at $T_s \geqslant 500\ °C$ ($T_s/T_m = 0.4$) anodize to form the nanotubular morphology, while those deposited at lower temperatures yield a disordered morphology. Since this effect of temperature has been reported previously, see also Figure S3, we choose to demonstrate the effect of pressure, Figure 2, to achieve the same end goal and hence