Thin Solid Films 558 (2014) 99–103

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

A combinatorial investigation of sputtered Ta–Al–C thin films

Mark D. Tucker [a,b,*], Marcela M.M. Bilek [a], David R. McKenzie [a]

[a] School of Physics, The University of Sydney, NSW 2006, Australia
[b] Thin Film Physics, Linköping University, 581 83 Linköping, Sweden

ARTICLE INFO

Article history:
Received 16 May 2013
Received in revised form 26 February 2014
Accepted 26 February 2014
Available online 11 March 2014

Keywords:
MAX phase
Tantalum
Combinatorial

ABSTRACT

We describe a combinatorial experiment investigating the Ta–Al–C material system, conducted with the aim of determining why the tantalum-containing $M_{n+1}AX_n$ phases have so far proved to be not amenable to thin-film synthesis. Samples were deposited onto (0001) Al_2O_3 wafers at 850 °C and characterized by X-ray diffraction wafer maps, scanning electron microscopy, and surface optical scattering. Elemental Ta, the binary phases TaC, Ta_2C, and $TaAl_3$, and the ternary phases Ta_3Al_2C and Ta_5Al_3C were identified. The morphology, phase composition and preferred orientation of the films deposited were found to be highly sensitive to the Ta fraction of the incident flux during deposition. No MAX phase material was observed, indicating that the Ta-containing MAX phases do not form under the deposition conditions investigated. Explanations associated with inadequate coverage of stochiometries, preferential sputtering, and thermodynamic instability have been ruled out. An explanation based on reduced surface diffusion of Ta during growth is proposed. A substantially higher substrate temperature during deposition is likely to be required to synthesize Ta-containing MAX phases.

1. Introduction

The tantalum $M_{n+1}AX_n$ (MAX) phases are of fundamental interest as tantalum has the largest atomic mass of any of the transition metals that form MAX phases, and so the Ta MAX phases have some extreme properties among these materials. Experimental investigations of bulk Ta_2AlC and Ta_4AlC_3 [1,2] have found and reported the highest bulk moduli of the MAX phases, and the elastic constants of several of the Ta-containing MAX phase structures are predicted to have extreme values [3].

The MAX phases Ta_2AlC, Ta_3AlC_2 and Ta_4AlC_3 have been synthesized by bulk high-temperature methods [1,2,4,5] and by crystal growth in a molten Al solvent [6]. These phases have not, however, been reported as thin films although thin film synthesis has been attempted [7]. More generally, there have been no reports of the thin film synthesis of any MAX phases with a period 6 transition metal, Ta and Hf being the two possibilities. It has been suggested that the apparent difficulty of growing these phases as thin films could be a consequence of the high atomic mass of Ta and Hf, resulting in increased resputtering of the deposited film by Ar atoms reflected off the transition metal target [7].

We describe experiments conducted with the aim of determining whether the tantalum MAX phases form as thin films using magnetron sputtering, under conditions similar to those used for the deposition of other MAX phases. In particular, we aim to determine whether resputtering is a process that shifts the composition of the deposited material preventing formation of the MAX phase. To efficiently explore a wide range of Ta–Al–C compositions we used a combinatorial method, where a range of compositions are synthesized simultaneously. Combinatorial methods are widely used for investigations of large parameter spaces, and have a long history of use in thin-film research on ternary material systems [8–10].

2. Experimental methods

Samples were deposited using a sputtering system fitted with four 76 mm circular magnetrons positioned symmetrically around the substrate in a confocal arrangement. Three elemental targets, Ta, Al, and C (graphite), were used. The Al and C targets were mounted in opposite magnetrons, and the Ta target in one of the remaining magnetrons; the fourth magnetron was not used. The Al and Ta targets were sputtered using DC bias; the C target was sputtered using RF bias. All three supplies were operated in power regulating mode.

To produce a composition gradient across the substrate, a square shield was installed in the chamber in front of the substrate, as shown in Fig. 1. Trial tantalum depositions were made, varying the size and position of the shield, and surface profilometry was used to assess the resulting film thickness gradients. The shield size and position shown in Fig. 1 produced the largest and most linear thickness gradient across the substrate of the geometries tested.

The thickness deposition rate as a function of position across the substrate was determined for each magnetron target by depositing test samples at ambient temperature and making stylus profilometer thickness measurements at a grid of points on the sample surface.

* Corresponding author at: Imaging and Applied Physics,Curtin University Kent St, Bentley WA 6102, Australia.
E-mail address: mark.tucker@liu.se (M.D. Tucker).

http://dx.doi.org/10.1016/j.tsf.2014.02.086
0040-6090/

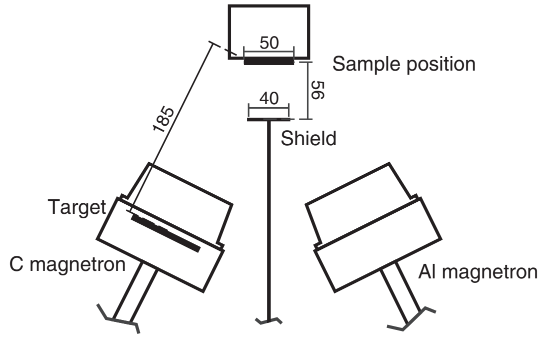

Fig. 1. The positions of two of the magnetron sources, the substrate and the deposition shield in the sputtering chamber. The magnetron containing the Ta target is not shown. Dimensions are in mm.

Quartz crystal monitor (QCM) measurements were made to determine the film density and deposition rate as a function of magnetron power for each target.

Following these calibration steps, four Ta–Al–C samples were made at magnetron power levels chosen to produce a sample set covering the area of interest in the Ta–Al–C incident composition space. For the Ta and Al targets, the power values used were in the ranges 60–170 W and 30–240 W respectively. For the C target, 600 W was used for all samples. The substrates used were polished single crystal (0001) oriented Al_2O_3 wafers of 50 mm diameter. The substrate was clamped to a sample holder held at 850 °C during deposition. Sputtering was carried out with Ar at a pressure of 2.5 mTorr (0.33 Pa). Each deposition was for 60 min. The base pressure in the chamber, after heating the sample, was less than 5×10^{-6} Torr (7×10^{-4} Pa); the oxygen content of one of the samples was subsequently measured using X-ray photoelectron spectroscopy and found to be below 2 at.%.

X-ray diffraction (XRD) wafer mapping measurements in θ–2θ geometry were made using a Philips X'Pert MRD diffractometer equipped with a sample stage with x and y translation. The illuminated spot on the sample, using line focus with an x-ray mirror, was of dimensions 5 mm × ~1 mm. Scans over the 2θ range 5°–95° were taken on a 3 × 3 point grid across each sample, with adjacent points separated by a distance of 15 mm. Scans over the smaller 2θ range 34°–48° were then taken on a finer 9 × 9 point grid, with adjacent points separated by a distance of 5 mm. This smaller 2θ range was chosen to include the main peaks seen in the previous scans.

Areas of the deposited films where the Al fraction of the incident flux was low had a specular visual appearance, whereas areas where the Al incident flux was higher scattered incident light. To investigate these variations, photographs were taken of the samples using a camera positioned with its axis normal to the sample surface. The sample was illuminated with an electronic flash at oblique incidence to the sample surface. With this arrangement, regions of the sample where light is scattered at the surface appear as light areas in the image, and both specularly reflecting and absorbing regions of the sample appear as dark areas.

Scanning electron microscope (SEM) images were acquired using a Zeiss EVO 50 SEM, operated at 15 kV. Images were acquired in plan view, and with a 30° sample tilt in some areas to reveal the surface topography.

3. Results

XRD scans extracted from the wafer maps for the 2θ range 34°–48° are shown in Fig. 2. The scans shown were chosen to include all the peaks seen in the complete wafer map dataset. Two binary carbides were found: TaC (the cubic monocarbide) and Ta_2C (the hcp subcarbide). Several peaks corresponding to the intermetallic tetragonal phase $TaAl_3$ are present. The (non-MAX phase) ternary compounds Ta_5Al_3C and Ta_3Al_2C are present in small regions. Finally, bcc α-Ta was found, the usual phase of bulk Ta. A low intensity background peak is present in the scan at incident composition $Ta_{21}Al_{62}C_{17}$ as this scan was at a point near the edge of the wafer.

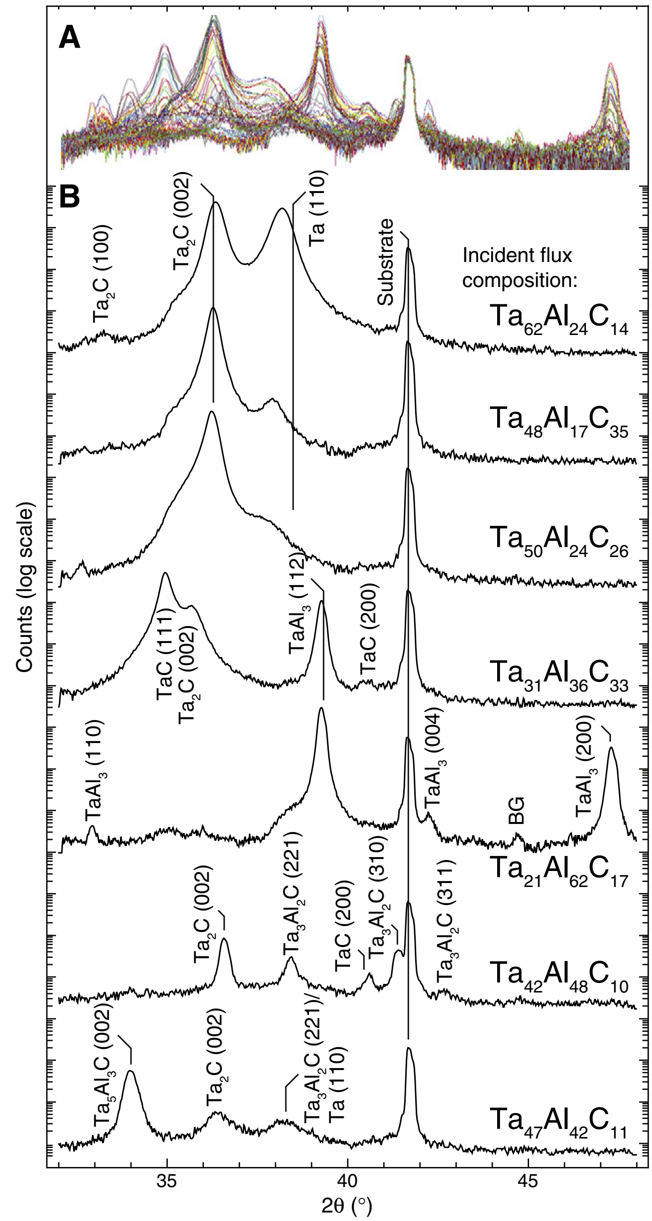

Fig. 2. a) The data of one of the 81-scan XRD wafer maps. b) θ–2θ XRD scans taken at points of the indicated incident compositions, extracted from the 81-scan wafer maps. Note that the incident composition is not necessarily the film composition. The scans shown were chosen to include all the peaks seen in the complete dataset. 'BG' in the $Ta_{21}Al_{62}C_{17}$ scan is a background peak from the sample stage.

The scans over the 2θ range 5°–95° (not shown) did not indicate the presence of any additional phases. In particular, the distinctive (00l) MAX phase peaks at low 2θ angles did not appear in any of the scans.

To further investigate patterns in the composition-space distribution of the phases identified, a list of peak heights and positions was compiled from the XRD data. A principal set of peaks were selected for analysis: α-Ta (110), TaC (111), Ta_2C (002), $TaAl_3$ (112) and (200), Ta_3Al_2C (111), and Ta_5Al_3C (002). The XRD peak intensity as a function of wafer position was combined with the incident composition versus wafer position to generate Fig. 3, where XRD peak intensities are plotted as a function of incident composition. In this figure, the region of the incident composition space where a particular phase is found is indicated