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Chromium aluminium nitrides thin films prepared with an atmospheric pressure plasma processing

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Abstract: The sol-gel derived thin films were coated on quartz and then bombarded with an atmospheric pressure plasma using N_2 (99.995%) for 10 min. Cubic CrN phase is observed up x=0.8. Moreover, the lattice parameter of the thin films monotonically decreased with x=0.5 above which the value did not change significantly. Hence, this work demonstrates that atmospheric pressure plasma processing provides an effective and fast route to prepare $Cr_{1-x}Al_xN$ thin films.

Keywords: CrN, chromium aluminium nitride, thin films, atmospheric pressure plasma.

1. Introduction

Transition metal nitrides have high melting point, excellent wear resistance, good corrosion resistance, good electrical properties, and good catalytic properties [1-3]. These superior properties of these nitrides are increasingly and applied to many applications. The nitrides have been applied to coatings for cutting tool, drill, and decoration for several decades. In the increasing demand, ternary transition metal nitrides are also developed rapidly [4, 5].

These nitrides deposited on substrates are frequently achieved with vacuum-based methods. Generally, physical vapor deposition (PVD) techniques have been applied extensively [6, 7]. Nevertheless, few investigations on non-vacuum techniques for the preparation of nitrides thin films are reported [8-12]. In our previous report, the chromium nitride thin films have been prepared using atmospheric pressure plasma process [13, 14]. Hence, a facile approach for preparing chromium aluminium nitride ($Cr_{1-x}Al_xN$) thin films with an atmospheric pressure plasma process is reported.

2. Experimental details

Thin films coated on quartz substrate were performed by a spin coater using precursor containing chromium and aluminium sources. $Cr(NO_3)_3•9H_2O$ (purity 98%+, SHOWA) and $Al(NO_3)_3•9H_2O$ (purity 98%+, PANREAC) were dissolved in 25 mL ethanol (95%), and 0.05 mol triethanolamine (purity 95%+, Tedia, USA) was then added to the solution to form a precursor. The precursor was stirred and aged for four days and then coated onto quartz substrates at 1500 rpm for 15 s. After that, the specimens were dried at 180℃ for 10 min in ambient. An atmospheric microwave plasma torch system [13, 15] operated at 1100 W was employed to prepare $Cr_{1-x}Al_xN$ thin films. The specimens were placed at 5 cm below the bottom of resonance cavity throughout this study. The bombardment duration from plasma ignition to turn-off was 10 min and then cooling with swirl gas for 10 min. The flow rate of the swirl N_2 (99.995%) was fixed at 9 L/min and the axial gas was fixed at 1 L/min using N_2 (99.995%). The temperature was measured with a S-type thermocouple and connected to a personal computer via RS-485 interface.

The crystal structure of the thin films was detected by the X-ray diffractometer (Bruker D8 Discover SSS) with Cu-Kα radiation (λ=0.154 nm) operating at 40 kV and 40 mA. The operated mode was grazing incidence with an incidence angle 1° and sampled step size was 0.02° within 2θ=10-70°. The lattice parameters of the thin films were refined using TOPAS package (Total Pattern Analysis Software, Bruker AXS) after obtaining the X-ray diffraction pattern. The surface morphology of the sol-gel derived thin films annealed using atmospheric pressure was analyzed by a field emission scanning microscope (FE-SEM, JEOL JSM-6700F). Moreover, the chemical composition of Cr and Al in the thin films was measured using an energy dispersive spectroscopy (EDS).

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction pattern of sol-gel derived specimens bombarded with atmospheric pressure plasma using axial N_2 (99.995%) for 10 min at 5 cm. Two terminal phases, CrN (JCPDS #11-0065) and cubic-AlN (c-AlN, JCPDS #25-1495), are also given in the top of the figure. Three intense diffraction peaks were found at x=0.0 after atmospheric pressure plasma bombardment, which are assigned as CrN (110), CrN (200), and CrN (220), respectively. These three diffraction peaks are remained with Al contents in thin films, which could reveal that no other phases is formed. This indicates that Al might complete dissolve in the CrN host phase to form $Cr_{1-x}Al_xN$ thin films. Our observation is consistent with the thin films deposited using cathodic arc evaporation [6].

Fig. 1(b) illustrates the lattice parameter of $Cr_{1-x}A_{lx}N$ thin films, where two dashed lines in the figure represent the lattice parameter of the terminal CrN (JCPDS #11-0065) phase and c-AlN (JCPDS #25-1495) phase. The lattice parameter of obtained CrN thin films (at x=0.0) is consist with that deposited using vacuum-based methods [6] although its value is slightly higher than that reported in JCPDS database (JCPDS #11-0065). Additionally, the lattice parameter of $Cr_{1-x}Al_xN$ thin films falls between the value of CrN and c-AlN phase and are gradually decreases at x=0.5 where reaches nearly the lattice parameter of c-AlN phase. Above that, the lattice parameter of the thin films gradually increased but retained between the value of CrN and c-AlN phase.

A series of surface morphologies of sol-gel derived thin films containing various Al contents after atmospheric pressure plasma bombardment is displayed in Fig. 2. From the micrographs, the surface morphology of the CrN thin films (at x=0.0) exhibits feature of granular, large particle-like, and rough surface. However, the surface turns to granular but small particle-like morphology with Al contents increasing in $Cr_{1-x}Al_xN$ thin films. Additionally, a compact and dense surface can also be observed between the Al content of 30% and 50% in the thin films. It is noted that the surface became nano-granular feature as the Al content in the thin films above 60%. The thickness of $Cr_{1-x}Al_xN$ thin films in the present work was in the range of 150 nm to 530 nm.

Moreover, the Al concentration in $Cr_{1-x}Al_xN$ thin films was detected from the energy dispersive spectroscopy (EDS) and was then calculated using [Al]/([Al]+[Cr]), where [Al] and [Cr] are the concentration acquired from EDS measurements. Fig. 3 shows the Al concentration in the thin films versus that calculated in the precursor. The Al contents in the thin films showing a near linear correlation with that in precursor is observed. This indicates that the stoichiometry in $Cr_{1-x}Al_xN$ thin films can be easily assigned during the precursor preparation.

4. Conclusion

In this work, $Cr_{1-x}Al_xN$ thin films are prepared using atmospheric pressure plasma process for 10 min from plasma ignition to turn-off. $Cr_{1-x}Al_xN$ thin films can be formed using the axial N_2 (99.995%) at 1100W at 5 cm. The lattice parameter of $Cr_{1-x}Al_xN$ thin films between that of CrN and c-AlN phase is observed and is gradually decreases at x=0.5. Moreover, the stoichiometry of $Cr_{1-x}Al_xN$ thin films can be controlled during the precursor preparation. Hence, an atmospheric pressure plasma process provides a facile and fast route to prepare $Cr_{1-x}Al_xN$ thin films.

Acknowledgements

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5. References

[1] X. Peng, C. Pi, X. Zhang, S. Li, K. Huo, P.K. Chu, Sustainable Energy & Fuels, **3** 366 (2019).

[2] S.A. Rasaki, B. Zhang, K. Anbalgam, T. Thomas, M. Yang, Progress in Solid State Chemistry, **50** 1 (2018).

[3] Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu, H.J. Fan, Adv Sci (Weinh), **3** 1500286 (2016).

[4] W. Sun, C.J. Bartel, E. Arca, S.R. Bauers, B. Matthews, B. Orvañanos, B.-R. Chen, M.F. Toney, L.T. Schelhas, W. Tumas, J. Tate, A. Zakutayev, S. Lany, A.M. Holder, G. Ceder, Nature Materials, **18** 732 (2019).

[5] A.L. Greenaway, C.L. Melamed, M.B. Tellekamp, R. Woods-Robinson, E.S. Toberer, J.R. Neilson, A.C. Tamboli, Annual Review of Materials Research, **51** 591 (2021).

[6] A.E. Reiter, V.H. Derflinger, B. Hanselmann, T. Bachmann, B. Sartory, Surface and Coatings Technology, **200** 2114 (2005).

[7] G.G. Fuentes, L. Pérez-Gandarilla, A. Medrano, J. Fernández Palacio, R. Bueno, E. Arias-Egido, J. Fernández, Surface and Coatings Technology, **420** 127326 (2021).

[8] R.P. Cardoso, G. Arnoult, T. Belmonte, G. Henrion, S. Weber, Plasma Processes and Polymers, **6** S302 (2009).

[9] Y. Yoshimitsu, R. Ichiki, K. Kasamura, M. Yoshida, S. Akamine, S. Kanazawa, Japanese Journal of Applied Physics, **54** 030302 (2015).

[10] A. Straboni, L. Pichon, T. Girardeau, Surface and Coatings Technology, **125** 100 (2000).

[11] H. Nagamatsu, R. Ichiki, Y. Yasumatsu, T. Inoue, M. Yoshida, S. Akamine, S. Kanazawa, Surface & Coatings Technology, **225** 26 (2013).

[12] R. Ichiki, M. Kono, Y. Kanbara, T. Okada, T. Onomoto, K. Tachibana, T. Furuki, S. Kanazawa, Metals, **9** 714 (2019).

[13] H.-Y. Chen, W.-H. Yang, Thin Solid Films, **706** 138095 (2020).

[14] H.-Y. Chen, W.-H. Yang, Surface and Coatings Technology, **391** 125688 (2020).

[15] H.-Y. Chen, J.-H. Ou, Materials Letters, **228** 81 (2018).

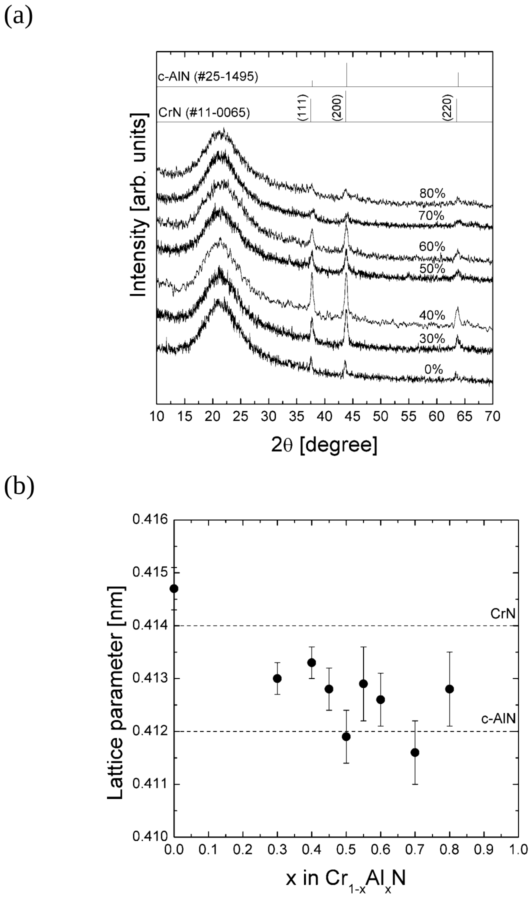

Fig. 1. (a) The X-ray diffraction pattern of the sol-gel derived thin films bombarded using atmospheric pressure plasma with axial N_2 (99.995%) for 10 min and (b) the lattice parameter of the obtained thin films determined by

TOPAS as a function of Al content in $Cr_{1-x}Al_xN$ thin films.

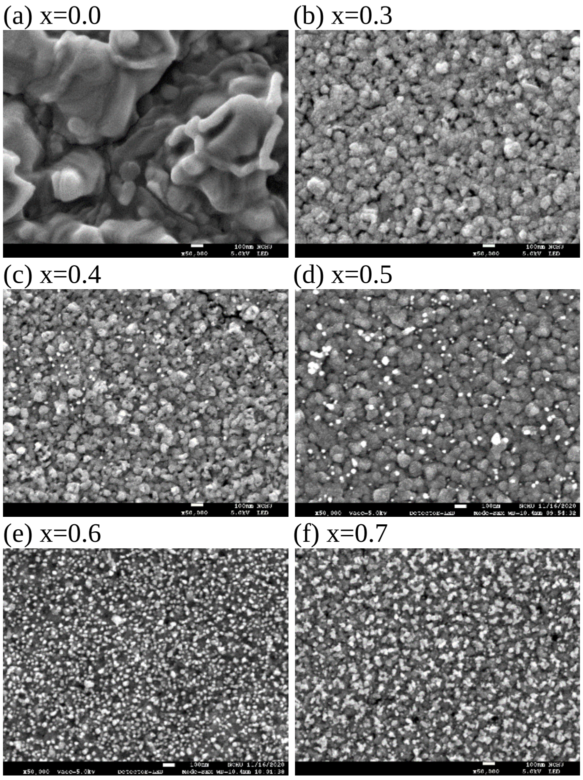
(a) x=0.0
(b) x=0.3
(c) x=0.4
(d) x=0.5
(e) x=0.6
(f) x=0.7

Fig. 2. The FE-SEM morphology of $Cr_{1-x}Al_xN$ thin films. (scale bar is 100 nm)

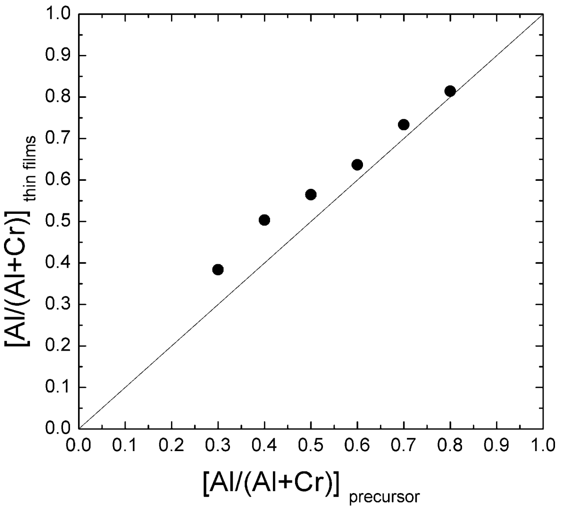

Fig. 3. The Al concentration in the thin films determined by EDS compares to that in the precursor.