Thermal stability of TiZrAlN films deposited by a reactive magnetron sputtering method

G. Abadias[1], I. A. Saladukhin[2], V.V. Uglov[2], S. V. Zlotski[2]

[1]*Institut P', Université de Poitiers-CNRS-ENSMA, SP2MI, Téléport 2, F86962 Chasseneuil-Futuroscope, FRANCE, gregory.abadias@univ-poitiers.fr*

[2]*Belarussian State University, 4 Nezavisimosti ave., 220030 Minsk, BELARUS, solodukhin@bsu.by*

Introduction

Quaternary TiZrAlN films are:

• perspective for both oxidation and wear resistance applications and expectant substitution for TiN, (Ti,Al)N and (Ti,Zr)N hard films [1-4];

• capable to possess by the unique properties due to possibility of nanocomposite structure formation during their synthesis [3, 5].

The aim of the present work is to study the thermal stability, under vacuum and air annealing, of quaternary transition metal nitride films, namely $(Ti,Zr)_{1-x}Al_xN$, with emphasis on the role of Al content on the structure and phase formation.

Coating growth conditions

$(Ti,Zr)_{1-x}Al_xN$ films with thickness of 300 nm have been deposited onto Si (001) wafers by a reactive unbalanced magnetron sputtering method. Titanium, zirconium and aluminum targets were co-sputtered under mixed $Ar+N_2$ plasma discharges at a total pressure in the working chamber equal to 0.20 Pa. Varying the RF power of the Al target from 20 to 200 W resulted in a concentration of aluminum x_{Al} in the films to increase from 2.6 to 36.4 at.%, while the Ti:Zr concentration ratio was kept constant to ~1.0.

Influence of Al concentration on phase formation and structure of as-deposited $(Ti,Zr)_{1-x}Al_xN$ films

Results of the XRD analysis on as-deposited films indicate the formation of (Ti,Zr,Al)N solid solution. However, with rising Al concentration, the structure changes from nanocrystalline to nanocomposite and then it turns into the amorphous state. This structural evolution is accompanied with a transition from (111) to (200) texture at low Al concentrations and by a subsequent displacement of the (Ti,Zr,Al)N diffraction peak to area of hexagonal AlN mononitride at the aluminum concentration $x_{Al} \geq 13.8$ at.%.

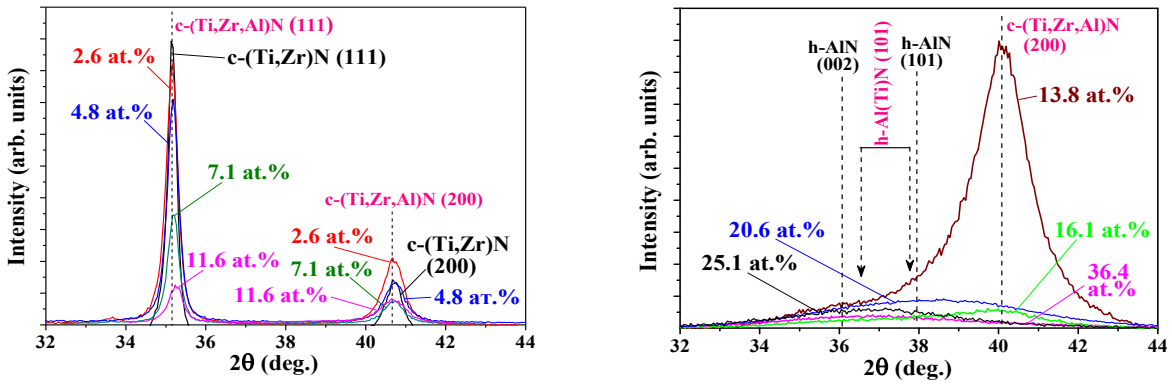

Fig. 1. Evolution of XRD patterns with Al content

Thermal stability of $(Ti,Zr)_{1-x}Al_xN$ films during annealing in air

Annealing under air atmosphere of the samples coated by $(Ti,Zr)_{1-x}Al_xN$ films was carried out for temperature intervals ranging from 400 to 950°C using in situ temperature XRD.

Corresponding to the (Ti,Zr,Al)N solid solution the diffraction lines disappear at T=600°C. At the same temperature (600°C), the initiation of a film oxidation process is observed. However, the intensive formation of orthorhombic $(ZrTi)O_4$ oxide phase occurs only at the temperature of 780°C.

Increase in x_{Al} up to 25.1 at.% leads to oxide formation reduction that can be explained by the passivating role of the Al_2O_3 surface layer.

Al target RF power supply (W)	[Ti] / ([Ti]+[Zr])	[Al] / ([Al]+[Ti]+[Zr]) (%)
30	0.52	4.8
60	0.52	11.6
80	0.52	16.1
120	0.51	25.1
200	0.50	36.4

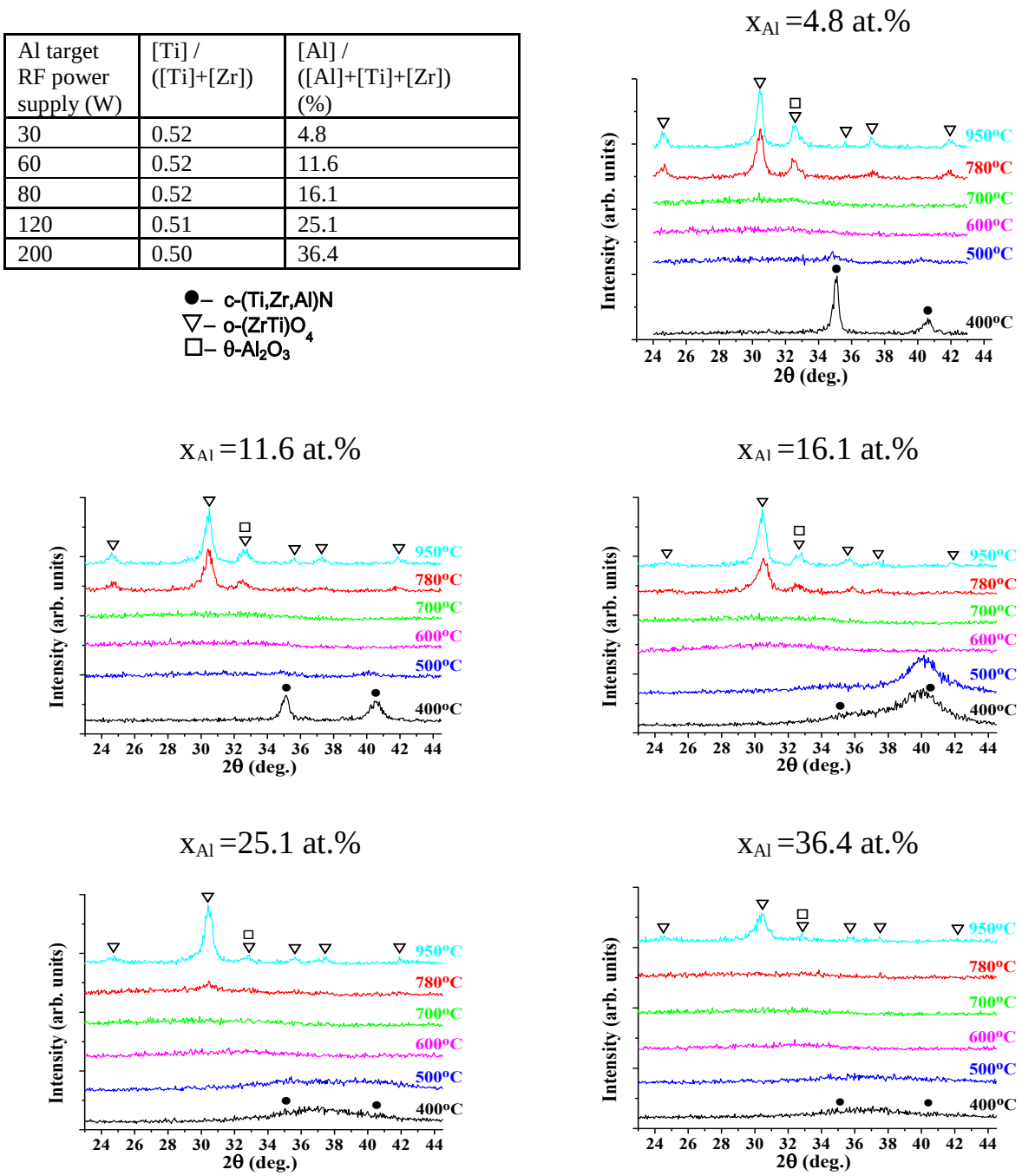

Fig. 2. Evolution of XRD patterns with annealing temperature increase

Thermal stability of $(Ti,Zr)_{1-x}Al_xN$ films under annealing in vacuum

Annealing in vacuum (~10^{-4} Pa) at the temperature of 600°C does not cause any essential change of (Ti,Zr,Al)N solid solution structure.

After annealing in vacuum at 950°C, the structure of the films depends essentially on the aluminum content. At the smaller Al concentrations, the (Ti,Zr,Al)N solid solution remains stable.

The TiN and ZrN mononitride phases become dominating when $x_{Al} \geq 13.8$ at.%. At the same time, aluminum is apparently included substitutionally into these phases by forming the solid solutions of TiAlN and ZrAlN type.

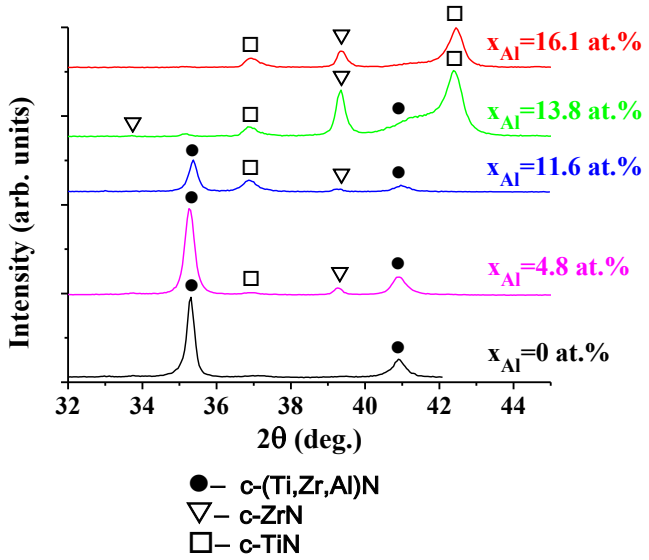

Fig. 3. Phase composition of $(Ti,Zr)_{1-x}Al_xN$ films after annealing in vacuum (950°C)

Conclusions

- With the increase of the Al concentration (x_{Al}) the structure of $(Ti,Zr)_{1-x}Al_xN$ films changes from nanocrystalline (c-(Ti,Zr,Al)N) to nanocomposite (c-(Ti,Zr,Al)N + + h-Al(Ti)N) and then to the amorphous state (a-(Ti,Zr,Al,N))
- Under annealing in air the films in a-(Ti,Zr,Al,N) state ($x_{Al} \geq 25.1$ at.%) are characterized by the highest oxidation resistance
- Under annealing in vacuum the (Ti,Zr,Al)N solid solution remains stable (at $x_{Al} \leq 4.8$ at.%) when the temperature changes from 600 to 950°C, and it decomposes onto mononitrides at higher Al concentration when the temperature reaches 950°C

References

1. L.Chen et al. Thin Solid Films **519** (2011) 5503
2. J. Zhang et al. Thin Solid Films **517** (2009) 4830
3. Y.J.Kim et al. Thin Solid Films **516** (2008) 3651
4. V.P.Tabakov et al. Russian Engineering Research **30/1** (2010) 84
5. G.Abadias et al. Reviews to Nanomeeting, Minsk, 24-27 May 2011, pp. 458-461.