Electronic Supplementary Material (ESI) for RSC Advances.

Table S1. Details of the deposition conditions of the $Ti_xM_{1-x-y}N_y$ unbalanced magnetron sputtered films.

Experimental Conditions	$Ti_{0.5}N_{0.5}$ films	$Ti_{0.25}Al_{0.25}N_{0.5}$ films	$Ti_{0.5}Al_{0.2}Si_{0.05}N_{0.5}$ films
Empirical formula	$Ti_{0.5}N_{0.5}$	$Ti_{0.25}Al_{0.25}N_{0.5}$	$Ti_{0.5}Al_{0.2}Si_{0.05}N_{0.5}$
Formula weight	30.947 g/mol	25.721 g/mol	25.776 g/mol
Substrate	AISI M2 steel	AISI M2 steel	AISI M2 steel
Target materials	Ti	Ti + Al	Ti + Al + Si
Reaction gas	Ar is working gas, N_2 is reactive gas	Ar is working gas, N_2 is reactive gas	Ar is working gas, N_2 is reactive gas
Substrate thickness	3 mm	3 mm	3 mm
Target to substrate distance	170 mm	170 mm	170 mm
Substrate temperature	500 ^oC	500 ^oC	500 ^oC
Substrate DC bias voltage	-50 V	-60 V	-55 V
Substrate holder rotation frequency	10 rpm	10 rpm	10 rpm
Ar flow rate	50 sccm	20 sccm	20 sccm
N_2 flow rate	Controlled by optical emission monitor (OEM) OEM = 60%	Controlled by optical emission monitor (OEM) OEM = 35%	Controlled by optical emission monitor (OEM) OEM = 35%
Ar partial pressure	0.133 Pa	0.133 Pa	0.133 Pa
N_2 partial pressure	0.04 Pa	0.106 Pa	0.106 Pa
(Ar + N_2) pressure	0.17 Pa	0.24 Pa	0.24 Pa
Operating pressure	0.17 Pa	0.24 Pa	0.24 Pa
Base/ultimate pressure	4×10^{-4} Pa	4×10^{-4} Pa	4×10^{-4} Pa
Ti target power	2 kW	2.2 kW	2 kW
Ti target current	8.0 A (DC)	6.0 A (DC)	6.0 A (DC)
Al target power	-	1.6 kW	1.2 kW
Al target current	-	6.0 A (DC)	4.5 A (DC)
Si target power	-	-	460 kW
Si target current	-	-	1.5 A (DC)
Deposition rate	~1.3 nm/min	~2.2 nm/min	~2.2 nm/min
Deposition time	150 min	90 min	90 min
Thickness of the films	~0.2 μm	~0.2 μm	~0.2 μm

Table S2. Fitting results of the XPS data of $Ti_xM_{1-x-y}N_y$ sputtered films for the core level binding energies.

Samples	Line	Bonding states	Binding energy (eV)	FWHM (eV)	Percentages of the component (%)
$Ti_{0.5}N_{0.5}$	Ti2$p_{3/2}$	TiN	455.2	1.4	40.6
		Ti_2O_3	456.8	1.6	27.8
		TiO_2	458.4	1.6	14.9
	Ti2$p_{1/2}$	TiN	460.7	1.2	6.9
		Ti_2O_3	461.5	1.1	6.9
		TiO_2	463.0	1.1	2.7
	N1s	TiN	396.8	1.3	76.9
		TiO_xN_y	397.6	1.4	15.4
		Free N_2 or N_2 surface adsorbates	399.0	1.3	7.6
	O1s	O_2/TiN or TiO_2	530.5	1.1	29.3
		O_2/Ti	531.6	1.3	49.1
		TiON	532.8	1.3	21.6
$Ti_{0.25}Al_{0.25}N_{0.5}$	Ti2$p_{3/2}$	TiN/TiAlN	455.1	1.6	18.0
		Ti_2O_3	456.7	1.7	38.5
		TiO_2	458.5	1.6	16.6
	Ti2$p_{1/2}$	TiN/TiAlN	460.4	1.0	1.3
		Ti_2O_3	461.3	1.6	12.7
		TiO_2	463.2	1.6	12.8
	Al2p	AlN	74.2	1.0	69.4
		Al_2O_3	75.0	1.0	30.6
	N1s	TiN/TiAlN	396.5	1.3	45.7
		AlN	396.9	1.3	50.1
		TiO_xN_y and/or $TiAlO_xN_y$	398.5	1.0	4.2
	O1s	O_2/TiN or TiO_2	530.4	1.6	36.1
		O_2/Ti or O_2/Al	531.7	1.3	33.0
		TiON	532.6	1.3	30.9
$Ti_{0.5}Al_{0.2}Si_{0.05}N_{0.5}$	Ti2$p_{3/2}$	TiN/TiAlN	455.1	1.1	35.0
		Ti_2O_3	456.6	1.5	22.9
		TiO_2	458.6	1.7	15.3
	Ti2$p_{1/2}$	TiN/TiAlN	460.8	1.0	14.8
		Ti_2O_3	461.6	1.1	8.4
		TiO_2	463.1	1.1	3.5
	Al2p	AlN	74.1	1.2	74.5
		Al_2O_3	75.1	1.2	25.5
	Si2p	Si_3N_4	101.7	1.5	59.8
		O_2/Si or SiO_2	102.7	1.5	40.2
	N1s	TiN/TiAlN	396.8	1.1	44.8
		AlN	397.4	0.8	51.6
		TiO_xN_y and/or $Ti(Al/Si)O_xN_y$	398.4	0.8	3.6
	O1s	O_2/TiN or TiO_2	530.3	1.3	51.2
		O_2/Ti or O_2/Al or O_2/Si	531.5	1.3	33.9
		TiON or SiO_2	532.6	1.2	14.9