NOVEL NANOCOMPOSITE COATINGS

Advances and Industrial Applications

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To Jitka, Ellen, and Sophie

Preface

The field of plasma-based thin film processing has grown rapidly over the past two decades. The coating technology evolved and developed in many industries, including tooling industry and electronic or manufacturing industry. In all these fields, thin films have found their usage as decorative and metallurgical films, diffusion barriers in microelectronics, films for high-temperature applications, and cutting or forming applications. Indeed, plasma processing technology has a number of manifestations, from simple dc to pulsed glow discharges over microwave and rf plasmas to arc discharges of very specific characteristics. Due to high versatility in depositing a wide range of materials under a great range of conditions combined with high deposition rates, the plasma processing technologies have become the most preferred technologies in the last few years. However, very complex relations between the film growth conditions, forming structures and properties of thin films have to be fully understood in order to prepare new film systems with optimized properties.

This book is intended to provide a perspective look at a range of thin film plasma processing technologies and give an overview on principles of the film formation so that the complex structure–property relation can be more easily and intuitively understood. The mean part of the book comprises a review on Si-containing nanocomposite films based on transition metal nitrides with a wide range of compositions, focused especially on the novel amorphous-like nanocomposite Me-Si-N films with a high (≥25 at.%) Si content. Two selected high Si-containing nanocomposites are compared for their mechanical and high-temperature properties to demonstrate the importance of the structure and phase composition on their thermal stability and resistance against oxidation.

This book is presented in six chapters. Following the introductory Chapter 1, which gives an overview of materials development from traditional polycrystalline coarse-grained bulk materials to thin nanocrystalline and nanocomposite films with enhanced properties, Chapter 2 comprises fundamentals of thin film processing using plasma discharges as the working medium. Principles of plasma discharges and plasma chemistry are introduced for a better understanding of the complexity of the plasma processing technology. Further in this chapter, fundamentals of physical sputtering related to the processes involved during thin film deposition from solid targets are discussed. An overview of various deposition techniques helps the reader to understand the advantages and limitations in sputtering of thin films with specific structures and properties. Chapter 3 summarizes basic principles of condensation of sputtered adatoms on the substrate surfaces and film formation. This chapter also considers the manipulation of the plasma sputtering environment to influence the microstructure and properties of thin films by varying the deposition conditions. Here, the addition of alloying elements and the effect of their segregation to surfaces and grain boundaries on the film structure and morphology is discussed in details. Moreover, the structure–property relations in hard films are discussed in this chapter. Chapter 4 introduces the present status of the basic research on Me-Si-N films with low and intermediate Si content (<25 at.%). Here, the synergetic effect of the silicon and nitrogen content on the structure, morphology, and phase composition of the films is discussed with mechanical and other physical properties of the films. Development of the nanocomposite structure is also correlated with residual stresses and thermal stability of the Me-Si-N films with various crystallite-to-amorphous phase volume fraction ratio. Furthermore, oxidation mechanisms and oxidation kinetics through very broad Si content range in the films is also presented. Chapter 5 is dedicated to the investigation of the novel nanocomposite Zr-Si-N films with high Si content (≥25 at.%). This chapter summarizes the development of the structure, elemental composition, chemical bonding, and phase composition as a function of increasing partial pressure of nitrogen used during film deposition. The findings are further correlated with residual stresses and mechanical and physical properties of the films. Main scope of this chapter is focused on the thermal stability and resistance to oxidation of the Zr-Si-N films showing very close relations with the volume fraction ratio between crystalline and amorphous phases forming the films. Chapter 6 deals with another transition metal nitride material alloyed with a high amount of silicon. The W-Si-N films deposited from an alloyed WSi_2 target serve for comparison with the Zr-Si-N films with the same silicon content so that the difference in their properties can be analyzed and fully understood. Realization of the important role of phase composition on film properties helps to select the right material combination and consequently, to improve the film behavior for high-temperature applications by selecting the right material combination. Relationships between deposition conditions and film properties are also discussed in details in this chapter. The reader can also get acquainted with basic techniques for thin film characterization including methods for analyzing mechanical properties of thin films, their structure, residual stresses, elemental and phase composition, thermal stability and resistance against oxidation, which are summarized in the Appendix of this book.

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Nomenclature

a-	amorphous
a	radius of the contact circle
a_D	deposition rate
at.%	atomic percent
A	neutral atom in basic state
A^+	positively ionized atom
A^-	negative ion
A^*	atom in an excited state
A_e	work necessary to the elastic deformation of the film
A_t	total work done by the load applied to the film
AB	molecule consisting of two atoms A and B
b	magnitude of the Burgers vector
B	magnetic field
c-	crystalline
C	capacitance
$C_{1,..,x}$	fitting constants
d	displacement
d	average grain diameter
dc	direct current
$d_{s\text{-}t}$	substrate-to-target distance
e	lattice strain
E	intensity of electric field
E^*	effective (reduced) Young's modulus
E_{bi}	energy delivered to the film by ion bombardment
$E_{bi\,min}$	minimum energy delivered to the film
E_f	Young's modulus of the film

E_i	Young's modulus of the indenter
E_i	energy of an incident particle
E_s	Young's modulus of the substrate
E_t	energy of a target particle
fcc	faced centered cubic
f_r	repetition frequency
$F(h_c)$	area function of the real indenter shape
G	shear modulus
h-	hexagonal
h	penetration depth
h_a	depression of a sample around the indentation
h_b	Boltzmann's constant
h_c	contact depth
hcp	hexagonal closed packed
h_f	film thickness
h_{oxide}	thickness of the oxidized layer
h_r	depth of residual impression
h_s	substrate thickness
h_t	maximum penetration depth
H	hardness
H_{max}	maximum hardness
H_{post}	hardness of sample after annealing
i_s	substrate ion current density
I_d	magnetron discharge current
J	ion current density
J_{AC}	interfacial energy
J_C	grain boundary energy
k	Hall–Petch slope
K	relative dielectric constant
K	shape factor
l_c	critical spacing between dislocations

L	indenter load
m	Schmid factor
m	mass
M_A	atomic weight
Me	transition metal
M_i	mass of an incident particle
M_t	mass of a target particle
nc-	nanocrystalline
p_{Ar}	partial pressure of argon
p_{N_2}	partial pressure of nitrogen
p_{N_2min}	minimum value of partial pressure of nitrogen
p_T	total pressure of sputtering gas
P	indenter load
P_t	maximum load
r	radius of the film-substrate curvature
R	erosion rate
R_a	mean surface roughness
S	sputtering yield
S	material stiffness
t_1	length of the negative pulse
$t_{reverse}$	reverse time
T	temperature
T_a	annealing temperature
T_c	critical temperature
T_{cr}	crystallization temperature
T_e	temperature of electrons
T_i	temperature of ions
T_m	melting temperature
T_{ox}	onset temperature of oxidation
T_r	onset temperature of recovery
T_s	processing substrate temperature

U	surface binding energy
U_d	magnetron discharge voltage
U_{fl}	floating potential
U_s	substrate bias
v	wave length of photons
v_i	velocity of an incident particle
wt.%	weight percent
W_e	elastic recovery
x	stoichiometry

Units and Symbols

°C	degree Celsius
amu	atomic mass unit
A	ampere
Å	ångström
cm	centimeter
eV	electronvolt
F	farad
g	gram
GPa	gigapascal
h	hour
Hz	hertz
kW	kilowatt
kJ	kilojoule
kHz	kilohertz
K	kelvin
keV	kiloelectronvolt
l	liter
mg	milligram
mN	millinewton
min	minute
mol	mol
mW	milliwatt
mm	millimeter
mm^2	square millimeter
mm^3	cubic millimeter
mA	milliampere
MeV	megaelectronvolt

MJ	mega Joule
MPa	megapascal
nm	nanometer
pF	pikofarad
Pa	Pascal
s	second
V	volt
W	watt
μm	micrometer
μs	microsecond
α	thermal expansion coefficient
α_f	thermal expansion coefficient of the film
β	peak broadening
β_c	peak broadening due to crystallite size
β_e	peak broadening due to lattice strain
δ	density of material
Δ	average grain boundary thickness
ΔE	differential energy of sputtered atoms
ΔH_f	enthalpy of formation
ΔJ	energy difference
Δm	mass difference
ΔN	differential flux of sputtered atoms
ΔT	temperature difference
$\Delta\sigma$	macrostress difference
ε_0	permittivity of free space
ϕ	angle between the directions of the applied stress and the normal to slip plane
λ	wave length
λ	angle between the directions of the applied stress and the slip plane
Ω	ohm
ν	Poisson's ratio