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NEXAFS N *K*-edge study of the bonding structure on Al/Si doped sputtered CrN coatings

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ABSTRACT

Chromium nitride (CrN)-based materials display broad applications as protective coatings for automotive, power generation and aerospace industries, in which surfaces are often subjected to wear and corrosion. By using an appropriate choice of dopant, one can further increase the mechanical hardness, corrosion and oxidation resistance of these coatings. In order to identify the effect of dopants on the structural evolution and surface electronic properties of CrN coatings, $Cr_{1-z}(Al/Si)_zN$ coatings were prepared by magnetron sputtering and then characterized via X-ray diffraction (XRD) and soft X-ray synchrotron radiation Near-edge X-ray Absorption Fine Structure (NEXAFS) studies around N *K*-edge. Higher degree of crystallinity of the coatings were identified through XRD studies. The bonding structure, of the doped CrN coating, was analyzed by Near-edge X-ray Absorption Fine Structure (NEXAFS) measurements performed around the N *K*-edge (390–450 eV) in the Auger electron yield (AEY) and total fluorescence yield (TFY) modes. NEXAFS analysis revealed Cr3*d*(Al3*p*/Si3*p*)N2*p* hybridizations in $Cr_{1-z}(Al/Si)_zN$ compositions and complex structure splitting via spin–orbit interaction of the Cr3*d* levels.

1. Introduction

Over recent years, chromium nitride (CrN_x) has been widely used as protective coatings to enhance the mechanical performance, wear and corrosion resistance of metal components in engineering applications [1]. Both the hardness and oxidation resistance of CrN_x coatings [2] can be improved via the introduction of doping elements, *e.g.* Si, Ti, Al, Ni [3–6]. The dopants enhance these properties by creating various defects, such as vacancies, atom substitution, cluster formation and deformation [3]. High resolution transmission electron microscopy (HRTEM) study on $Cr_{1-x}M_xN$ coatings has shown the existence of nanocrystalline grains surrounded by amorphous grain boundaries [7]. Thus, the grain size and grain boundaries are crucial in controlling the hardness and oxidation resistance of such coatings. Integration of silicon, aluminum or titanium into the CrN_x matrix resulted in the reduction of grain sizes to the nano-scale [8]. When scaling the grain size down to the nanoscale, the formation of dislocations becomes difficult and the hardness of the coatings is thereby predominantly controlled by the grain boundary characteristics [9].

In recent years, X-ray photoelectron spectroscopy (XPS) [10], NEXAFS and extended X-ray absorption spectroscopy (EXAFS) [11], nuclear magnetic resonance (NMR) [12] and infra-red (IR) spectroscopy [13] have been used for structural characterization and phase identification of hard coatings in an attempt to understand and control various factors governing their properties [14,15]. Katsikini et al. [14] performed NEXAFS studies on binary AlN, GaN and InN nitrides and found that the energy positions of the absorption edge (E_{abs}) of these materials were shifted monotonically towards the higher wavelength side with the atomic number of the

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cation. The electronic structure of plasma assisted pulse laser deposition (PLD) grown AlN, CrN and Cr-doped AlN thin films were investigated by X-ray absorption spectroscopy (XAS) and soft X-ray emission spectroscopy at the N *K*-edge [8] and results were compared with that of density functional theory (DFT) models. Since, the X-ray absorption spectroscopic method probes the unoccupied and occupied densities of states of a material on an element-specific and orbital angular momentum specific basis controlled by dipole selection rules, the spectra acquired at N *K*-edge represent the N2*p* conduction band and valence band partial density of states (PDOS). DFT calculations show that the AlN PDOS has been shifted to allow for the overlap of the main occupied 2*p* PDOS. An appreciable N2*p* PDOS was observed just above Fermi energy only for those nitrogen sites that are beside the Cr and whose 2*p* states hybridized with Cr unoccupied 3*d* levels. The hybridised unoccupied N2*p* density of states was seen in the TEY X-ray absorption spectra. Similar theoretical and experimental NEXAFS studies on β- and spinel SiAlON have also been performed by Tatsuni et al. [15]. The authors in that study pointed out that the local environments of Al are independent of the composition. The elastic constants of β-SiAlONs were found to decrease with the increase of Al-content, thereby causing lattice softening, which may affect mechanical performance [16]. Synchrotron radiation X-ray absorption spectroscopy was employed to realize the influence of particle size on the distributions of the metal atoms over the tetrahedral and octahedral sites of the spinels and a slight deviation from the bulk structure was noticed due to the effect of the surface on tiny particles [17].

NEXAFS technique is one of the most popular and powerful spectroscopies for the investigating the surface unoccupied electronic structure of transition metal nitrides because; (i) the NEXAFS spectra provide the density of states of the unoccupied molecular orbitals which are directly related to the structural and electronic properties of transition metal nitrides; (ii) the AEY and TFY modes of NEXAFS technique work by different detection limits that can be successfully used to distinguish the bulk and surface properties of the materials. In a previous report, NEXAFS spectroscopy was used to probe the differences in the electronic structure of CrN with Al and Si doping in terms of chemical shifts seen in the Al *K*-, Cr *L*-, and Si *K*-edges [18]. Incorporation of dopants was found to play a remarkable role in modifying the grain boundary morphology and surface chemistry of these coatings. In a recent work, NEXAFS data were collected to explore the electronic and surface properties of nickel doped Cr-nitrides and to elucidate the differences between the surface and bulk compositions around the absorption edges of $Cr_{1-y}Ni_yN$ coatings [19]. The appearance of direct *d*-bonds and an increase in peak intensities within the Cr *L*-edge spectra confirmed the possible variations in valence and a reduction in crystalline domains, while an enhancement of Ni *L* absorption edges intensity indicated an improvement in the coordination and effective charge of Ni atoms. Understanding the electronic and surface structure of transition metal nitride-based thin film coatings is therefore crucial from both an experimental and theoretical perspective. However, there has been very limited effort toward elucidating the effects of dopant elements on the electronic and surface structural evolution, and on the tailoring of the grain boundaries. A recent review [20] provides comprehensive eloborations about the *K*-edge features of the transition metal compounds. In this study, we have conducted X-ray diffraction (XRD) analysis and synchrotron radiation NEXAFS measurements over the nitrogen *K* edge (N *K*-edge) for a series of $Cr_{1-z}(Al/Si)_zN$ coating samples with increasing incorporation of aluminum and silicon. Both surface sensitive Auger electron yield (AEY) and bulk sensitive total fluorescence yield (TFY) modes were used to investigate the effect of dopant elements (Al, and Si) on the crystalline phase, surface structural evolution and local electronic bonding states of the coatings.

2. Experimental technique

Aluminum and silicon doped CrN coatings with general formula $Cr_{1-z}A_zN$ (A = Al, or Si, and *z* varies from 14.3 to 28.5 at%) were prepared via magnetron sputtering approach. A TEER UDP 650/4 closed field unbalanced magnetron sputtering system with four-target configuration (Teer Coatings Ltd., UK) was used to coat the films on AISI M2 tool steel substrates (hardened to a hardness of HRC 60). Table 1 presents details pretinent to the deposition conditions for the preparation of the coatings. Four elemental targets were installed in the coating system (2 Cr + 1 Al + 1 Si). Compositions of the coatings were adjusted by controlling the sputtering power applied to each target (Cr, Al, and Si). The deposited coatings were cleaned mechanically in an ultrahigh vacuum using a diamond needle file and tungsten-wire brush. The atomic percentages of elemental compositions of $Cr_{1-z}Al_zN$ and $Cr_{1-z}Si_zN$ coating systems have been outlined elsewhere [18]. X-ray diffraction (XRD) was employed for the structural analysis, phase identification and homogeneity of the coatings. A Bruker Advance D8 X-Ray Diffractometer equipped with a LynxEye detector was used for the XRD measurements of the samples. The XRD machine used Cu-K_α radiation (λ = 1.5406 Å), and was operated at a power of 40 kV and 40 mA at room temperature. The XRD tests of samples were performed in a 2θ geometry from 30° to 60° in steps of 0.01°. The soft X-ray (SXR) beam-line at the Australian synchrotron facility in Melbourne was utilized for the NEXAFS measurements of the coatings. Here, horizontally polarized soft x-ray radiation is produced from an undulator light source. The beamline, based around a plane diffraction grating monochromator (line spacing1200 lines/mm) is used to collimate and monochromatize the X-ray beam. The films were mounted onto a stainless steel sample-holder using double-sided carbon tape, and introduced into the ultra high vacuum endstation on the beamline. The base pressure in the system was of the order of 5×10^{-10} Torr. The N *K*edge NEXAFS data ($h\nu$ = 380–450 eV, 0.1 eV step size) were acquired at the "magic angle" [18], in which the angle between sample surface and electric field vector of the polarized x-rays is 55°. Two different, simultaneous, detection modes were used to measure the x-ray absorption signal: surface sensitive Auger electron yield (AEY), obtained by

Table 1
Details of the deposition conditions of the $Cr_{1-z}A_zN$ (A = Al, or Si, and *z* varies from 14.3 to 28.5 at%) unbalanced magnetron sputtered coatings.

Process parameters	Name/Values
Crystal system	Cubic
Space group	$Fm\bar{3}m(225)$
Substrate	M42 steel (HRC 60)
Target configuration	2 Cr + 1 Al + 1 Si
Reaction gas	Ar is working gas, N_2 is reactive gas
Substrate thickness	3 mm
Target to substrate distance	170 mm
Substrate temperature	500 °C
Substrate bias voltage	−80 V
Substrate holder rotation frequency	10 rpm
Ar flow rate	50 sccm
N_2 flow rate	50 sccm
Ratio of gas flow	N_2:Ar = 1:1
Ar partial pressure	0.133 Pa
N_2 partial pressure	0.04 Pa
(Ar + N_2) pressure	0.173 Pa
Operating pressure	0.18 Pa
Base pressure	4×10^{-4} Pa
Deposition rate	~13 nm/min
Deposition time	150 min
Thickness of the coating	2 μm