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Annealing effects on microstructural, optical, and mechanical properties of sputtered CrN thin film coatings: Experimental studies and finite element modeling

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ABSTRACT

Chromium nitride (CrN) coatings were deposited by magnetron sputtering onto Si(100) substrates. The coatings were then annealed at different temperatures (500–800 °C in steps of 100 °C) in air for 1 h. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), UV–Vis spectroscopy, nanoindentation tests and finite element modeling (FEM) were conducted in order to investigate their structural, morphological, optical and mechanical properties. XRD patterns show that the crystallinity of the CrN phase increases with the rise in annealing temperatures together with its preferred orientations along (111) and (200) diffraction planes. The lattice constants were slightly reduced from 4.19 to 4.11 nm at 800 °C. The lattice micorstrains and residual stresses were also reduced as the annealing temperatures rose as a result of reduced defects, dislocations and vacancies. Smooth grain-like surfaces with grain sizes ranging between ~50 and 250 nm were confirmed by FESEM micrographs. XPS studies indicated the existence of Cr and N on the coating systems. Optical studies showed that with the rise in annealing temperature of up to 700 °C, the solar absorptance of CrN coatings is increased from 61% to 89% and slightly decreased at 800 °C, while the optical band-gap energy dropped from 2.62 to 1.38 eV and slightly increased to 1.48 eV at 800 °C. A gradual increase of dielectric constants of CrN films were realized with the subsequent annealing progression. Nanoindentation results indicated that as the annealing progresses, the hardness and elastic modulus values are lowered.

1. Introduction

Physical vapour deposited (PVD) binary CrN coatings are considered to be very useful candidates in many industrial applications because of their thermal stability, good coating-to-substrate adhesion, abrasion resistance, excellent wear resistance, low friction coefficient, oxidation resistance, and ideal hardness and elastic modulus values [1–4]. CrN coatings also show higher oxidation resistance and exceptional corrosion resistance under deleterious environmental exposures such as high temperatures and high pressure [5]. In comparison to other transition metal nitride coatings (*e.g.*, TiN, and TiCN), CrN coatings offer superior thermal stability, corrosion resistance and better tribological performance. Consequently, CrN coatings have been widely used as

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protective coatings in drawing dies, cutting tools, moulds, grinding tools, piston rings, and various moving parts in mechanical equipment [6–9]. The effect of heat treatment on the mechanical properties and microstructural features of CrN/AlN thin film based coatings have been studied by Tien et al. [10]. CrN thin film coatings have been studied for many years because of their excellent mechanical performance, thermal properties and anti-oxidation behaviour [11].

The chemical composition, chemical bonding states, roughening kinetics, and mechanical properties of Al-doped TiN coatings which had been prepared by magnetron sputtering in an ($Ar+N_2$) gas mixture were studied *via* XPS, AFM and nanoindentation measurements [12]. Increased Al-dopants from 10 to 50 at.% reduces the grain size and surface roughness due to the nucleation process, but the mechanical properties of the TiN structure were improved due to a reduced grain size, which indicates a high density of grain boundaries [12]. A linear relationship between residual stress and hardness of single-phase thin film coating materials such as TiN [13], and CrN [14] synthesized by physical vapour deposition methods have been reported in earlier studies. The strengthening effect of transition metal nitride based films such as TiN and CrN with decreasing grain size, generally, follows the Hall–Petch relationship as described in Ref. [15].

The absorption of solar energy by a thin film coating is dependent on its electronic configuration, wavelength of light, and the surface topographies of the coatings such as pits, pores, and/or peaks. Absorption of light may also be responsible for the excitation of electrons to higher energy states, the vibrational and rotational motions of bonds, the chemical reaction and restructuring/breaking of the chemical bonds, and the ionisation of atoms or molecules [16]. The optical properties and thermal stability of spectrally selective CrAlN–CrAlON thin film based absorbing coatings have been investigated in Ref. [17]. To date, various types of absorbing surfaces such as interference-type, cermet coating, and absorber–reflector tandem have been successfully developed in order to improve their solar absorption [18–23]. Magnetron sputtering derived HfO*x*/Mo/HfO_2 thin film coatings exhibited extraordinary solar absorptance up to 0.923 [24]. High temperature solar absorption together with good thermal stability and oxidation resistance of CrAlN films have been reported in an earlier study [19].

The enhancement of the tribological and mechanical properties of magnetron sputtered Ti/TiN, Cr/CrN and TiCr/TiCrN thin film coatings have been reported by Ezazi et al. [25]. In their study, the authors described combining TiN and CrN phases into a single film and presented a solution for the damage mechanisms that degrade material properties. The elastic hardness of CrN, CrAlN, CrTiN, and CrAlTiN sputtered coatings were evaluated by their grain sizes [26]. An average hardness of 14.5 GPa was reported for the CrN phase while CrTiAlN coating with the most compact morphological features demonstrated the highest hardness of 22.0 GPa [26]. Among the existing transition metal nitrides, CrN thin film coatings have been extensively studied with respect to their structural features, morphological information, thermal and mechanical properties which are the key requirements for high-temperature applications [10,15,27–30].

Many studies have been undertaken which examine the structural, morphological, spectral selective, local electronic bonding states, optical, mechanical and tribological properties of CrN-based thin film coatings [31–37]. However, a comprehensive study investigating the impact of annealing temperatures on structural, morphological, and optical properties and providing a detailed mechanical analysis *via* experimental procedure and finite element modeling in one paper is still lacking. Therefore, in this paper, paramount attention has been paid to understanding the impact of annealing temperatures on structural, optical, dielectric, and mechanical properties of sputtered CrN thin film coatings. The nanoindentation method was used to probe the mechanical parameters of CrN coatings. The intrinsic hardness was estimated *via* experiment and by modeling the substrate effect and was related to the microstructural features of the coatings. Accordingly, the correlation between their mechanical properties, residual stress level, adhesive strength, and levels of load induced stress induced at the coating-substrate interface, was also examined.

2. Experimental

2.1. Film preparation technique

The UDP650 closed field unbalanced magnetron sputtering (Teer Coatings Ltd, UK) system was used to prepare CrN thin film coatings onto Si (100) substrates. Two vertically mounted pure Cr targets (purity 99.9%, size 345 mm × 145 mm × 8 mm) surrounded by a rotating substrate holder provides a uniform exposure for growing the coatings. Prior to coating, a background pressure of 0.4×10^{-4} Pa and the working gas pressure (during sputtering) of 0.4 Pa was maintained throughout the process. Ar (99.999%) was used as the working gas for sputtering with a fixed flow rate at 50 sccm, and N_2 (99.999%) was used as a reactive gas to form nitrides while the optical emission monitor (OEM) was used to control dynamically. The nitrogen reactive gas was injected near the substrate holder. The entire synthesis process was carried out without any external heating and keeping the target to a substrate distance of 17 cm. Advanced Energy Pinnacle Plus power supply, at a frequency of 250 kHz was used to control the bias voltage while a DC power supply (current mode) was used to control the target current supply. To coat the CrN films, 0.2 μm chromium adhesive layers were applied to promote the coating adhesion with a bias voltage of −80 V [38,39]. The total thicknesses of these coatings were $d = 1.8$ μm. Finally, the obtained sputtered CrN coatings were annealed from 500 to 800 °C in steps of 100 °C in air for 1 h. Elaborate details on the sample deposition parameters are outlined in Table 1.

2.2. XRD experiments

The XRD measurements of the samples were carried out using a Bruker AXS D8 Advance (Germany) with Cu-K_α radiation ($\lambda = 1.54$ Å). The XRD machine was operated at 40 kV and 40 mA coupled with a Lynx-eyed detector. The XRD patterns were collected in a 2θ (degree) geometry = 30–70 with a step size of 0.01°.

2.3. FESEM experiments

The morphological features of as-deposited and annealed CrN thin film coatings were analysed using a field-emission scanning electron microscope manufactured by Zeiss Neon 40EsB FIBSEM, an Oxford Instruments Inca X-act SDD X-ray detector.

2.4. XPS experiments

Elemental compositions of the CrN films were estimated *via* XPS measurements around the outermost 5 nm surface. The XPS data of CrN films before and after annealing were collected using a Kratos Axis Ultra XPS spectrometer (Manchester, UK) operated with an Al-K_α monochromatic radiation (photon energy = 1486.6 eV) source at a power of ~10 mA and ~15 kV. The XPS machine was equipped with a cold stage, and an Ar ion gun for etching the coatings. The analysis chamber was set at a uniform pressure of 2.9×10^{-9} Torr.