Thin films of hard cubic Zr$_3$N$_4$ stabilized by stress

MANISH CHHOWALLA* AND H. EMRAH UNALAN
Rutgers University, Ceramic and Materials Engineering, Piscataway, New Jersey 08854, USA
*e-mail: manish1@rci.rutgers.edu

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Hard, refractory thin films consisting of group IVB element mono-nitrides deposited using various chemical and physical vapour-deposition techniques are widely used in wear-resistant applications. As the demand for performance exceeds the capabilities of existing materials, new materials with superior properties must be developed. Here we report the realization and characterization of hard cubic Zr$_3$N$_4$ (c-Zr$_3$N$_4$) thin films. The films, deposited using a novel but industrially viable modified filtered cathodic arc (FCA) method, undergo a phase transformation from orthorhombic to cubic above a critical stress level of 9 GPa as determined by X-ray diffraction and Raman spectroscopy. The c-Zr$_3$N$_4$ films are significantly harder (~36 GPa) than both the orthorhombic Zr$_3$N$_4$ (o-Zr$_3$N$_4$) and ZrN films (~27 GPa). The ability to deposit this material directly onto components as a thin film will allow its use in wear- and oxidation-resistant applications.

In addition to wear applications, nitride thin films are also widely used as brass-coloured decorative layers. Plasma-deposited nitride thin films (specifically zirconium nitride, ZrN) with superior hardness and corrosion resistance offer an environmentally friendly alternative to wet plating where a large amount of hazardous waste is generated. Nitride thin films such as TiN, ZrN, CrN and (Ti,Al)N are widely deposited at low temperatures (<400 °C) on an industrial scale using magnetron sputtering or cathodic arc plasmas. Mono-nitride thin films adopt the NaCl structure and are highly conductive owing to a finite density of states at the Fermi level from the residual electron contributed by each atom in the metal d band.

Although it is generally difficult to vary the concentration of nitrogen in nitride thin films, metastable higher nitrides with a composition of M$_3$N$_4$ (where M is either Hf or Zr) and orthorhombic structure have also been reported. These nitrogen-rich films are transparent and much less conducting than the mono-nitrides. Bulk samples of high-density cubic Zr$_3$N$_4$ and Hf$_3$N$_4$ (c-M$_3$N$_4$) with thorium phosphide (Th$_3$P$_4$) structure have been synthesized by Zerr et al. using a high-pressure laser-heated diamond anvil cell. Their results showed that the c-Zr$_3$N$_4$ formed at a pressure of 15.6–18 GPa and temperature of 2,500–3,000 K whereas the c-Hf$_3$N$_4$ phase could be obtained at 18 GPa and 2,800 K. The transition metal M$_3$N$_4$ phases are similar to the group IVA element nitrides (M$_3$N$_4$ where M = Si, Ge, Sn), which also show low- and high-density phases. The high-density γ phases of these nitrides with spinel structure, which are comparable to the c-M$_3$N$_4$ of transition metal nitrides, show extraordinary mechanical and electrical properties, which make them useful in many applications ranging from abrasives to material for blue LEDs. Following the experimental result of Zerr et al., several theoretical studies have been undertaken to understand and explore new properties of different phases of M$_3$N$_4$. The calculations indicate these new materials have extraordinary oxidation resistance and are expected to be nearly as hard as γ-Si$_3$N$_4$ and also semiconducting with a bandgap of around 1.5 eV. Indeed, Zerr et al. reported a high bulk modulus of 250 GPa for both c-Zr$_3$N$_4$ and c-Hf$_3$N$_4$ indicating high hardness and they also found that c-Hf$_3$N$_4$ was transparent.

In this work, we describe the deposition and characterization of cubic Zr$_3$N$_4$ thin films. These novel thin films were deposited using a novel modified filtered cathodic arc (FCA) where the metal vapour, generated by an arc discharge on pure zirconium cathode, was...
reacted with fully ionized atomic nitrogen. The plasma conditions generated by our modified FCA are unique and allow unprecedented control over the ion energy and flux. The zirconium nitride thin films deposited using our technique have Zr$_3$N$_4$ stoichiometry in contrast to films deposited by unmodified FCA, which are ZrN. The structure of our Zr$_3$N$_4$ films was determined by X-ray diffraction (XRD), electron diffraction in transmission electron microscope (TEM) and by Raman spectroscopy. Thin films were deposited at several ion energies with modified and unmodified FCA. Our results indicate that the cubic Zr$_3$N$_4$ is obtained at optimum ion energy ranging from 100–200 eV, which also correlated to the most highly stressed films. The compressive stress appears to be the key factor in obtaining the cubic versus the orthorhombic structure for Zr$_3$N$_4$. That is, films with Zr$_3$N$_4$ stoichiometry but with stress less than ~9 GPa have the orthorhombic crystal structure, whereas higher stress values yield the cubic structure. The hardness of the cubic Zr$_3$N$_4$ films measured using nano-indentation was found to be substantially higher (~36 GPa) than for films with orthorhombic or NaCl structures (~27 GPa). The films were also transparent with an absorption edge at around 1.6 eV.

Cathodic arc is an important source of highly ionized and directed plasma beams for energetic deposition of thin films. The high level of ionization in the plasma allows for precise control of the ion energy by applying a bias to the substrates. The ability to control the ion energy allows tunability of the thin-film structure. A quarter torus magnetic solenoid is generally used to filter out microscopic particles (referred to as ‘macro-particles’) that are also generated during the arc discharge. Thus the filtered plasma at the exit of the plasma duct is essentially free of macro-particles, allowing the deposition of atomically smooth, high-quality thin films. Although the metal vapour in FCA is completely ionized, the degree of ionization of the reaction gas (nitrogen in the case of nitrides) is relatively small (~10%). The lack of ionization leads to inefficient reactions and also broadens the ion-energy distribution of the impinging flux.

We have used a modified FCA process, which leads to a fully ionized plasma consisting of singly charged Zr$^+$, N$^+$ and ZrN$^+$ species to obtain the c-Zr$_3$N$_4$ phase. The modified method is similar to the unmodified FCA in all respects except that the nitrogen gas inlet into the chamber is by a 1-mm hole in the Zr cathode on which the reactive gas at the arc spot in order to enhance the formation of zirconium nitride on the cathode surface (referred to as poisoning). By adjusting the flow rate and pressure of the gas, it is possible to consume all of the nitrogen in the poisoning reaction. The poisoning of the cathode surface means that the arc discharge occurs on a nitride surface rather than pure Zr metal. The degree of poisoning is significantly enhanced in our modified FCA and thus our plasma characteristics show only singly charged Zr$^+$, as reported by Zerr et al. and others.

### Table 1 Comparison of c-Zr$_3$N$_4$ calculated and measured XRD peak positions as well as spacings measured by electron diffraction.

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Figure 1 Mass spectrum and ion-energy distribution (inset) of Zr-N plasma produced by the modified filtered cathodic arc. Three distinct mass peaks attributed N$^+$, Zr$^+$ and ZrN$^+$ charge states can be clearly observed. The Zr$^+$ and ZrN$^+$ mass peaks can be deconvoluted into three peaks associated with the most prevalent isotopes of Zr: The possibility of N$_2$$^+$ peak contributing to the N$^+$ peak was eliminated by closely monitoring the peak at 14.5 AMU from the $^{15}$N isotope. The absence of the 14.5 AMU peak indicates the peak at 14 AMU is entirely from N$^+$. Note that the intensity is in linear scale. The narrow ion-energy distribution of the Zr$^+$ species in the inset reveals a peak energy of ~18 eV. The N$^+$ and ZrN$^+$ species also exhibited similar energy distribution. The plasma characteristics were measured using a Hiden EQP Analyzer equipped with mass spectrometer located at the exit of a Hiden EQP Analyzer equipped with mass spectrometer located at the exit of the plasma duct is essentially free of macro-particles.
Figure 2 Crystal structures, XRD, TEM, Raman and UV-VIS spectroscopy data for various Zr-N thin films investigated in this study. Crystal structure of a ZrN based on the rock salt NaCl structure; b, orthorhombic Zr3N4 based on the space group Pnam; and c, the cubic Zr3N4 structure based on the I43d space group. d, TEM image of 100-nm c-Zr3N4 thin films deposited on salt. The TEM samples were produced by dissolving the salt in de-ionized water. The images were obtained using a JEM 2000FX TEM operated at 200 kV. The inset shows the electron diffraction pattern used to calculate the 2θ values in Table 1. e, XRD patterns from three types of Zr-N films produced by the filtered cathodic arc. The XRD was performed, using a Siemens MRD diffractometer with a Cu source, on 0.75-μm thin films deposited on Si substrates. In order to enhance the signal from the thin films, all measurements were performed at low grazing angles. The Si peaks from the XRD spectra have been removed for clarity. f, Raman spectrum of c-Zr3N4 thin films measured using a Renishaw Raman microscope with 514.5 nm Ar laser. The inset shows the Raman spectrum for ZrN films. g, Typical optical absorption properties of c-Zr3N4 deposited on quartz substrates. The absorption was measured using an UV-VIS spectrometer (Phillips two beam) with wavelengths in the 200 to 900 nm range.
N⁺ and ZrN⁺ species (Fig. 1) as expected from an arc discharge on Zr-N. That is, the arc evaporates Zr-N and then through collisions the compound is ionized or dissociated into Zr and N, which can be ionized through additional collisions. The narrow ion-energy distribution of the plasma is shown in the inset of Fig. 1. The fully ionized plasma with a narrow ion-energy distribution function provide significantly better control over the deposition parameters than previously reported of Zr-N plasmas²⁹, which we believe is essential for creating conditions for the formation of the metastable c-Zr₃N₄ phase.

The stoichiometry of all films deposited using the modified FCA was measured by Rutherford backscattering and found to be Zr₃N₄, whereas the unmodified FCA yielded only the mononitride. The oxygen content in the film was negligible. The three zirconium nitride crystal structures (rock salt, orthorhombic Zr₃N₄ (o–Zr₃N₄) and cubic Zr₃N₄) encountered in this study are shown in Fig. 2a–c. The TEM image of our polycrystalline films with crystallite sizes ranging from 100 – 200 nm is shown in Fig. 2d. The electron diffraction pattern is shown in the inset of the image and the spacings measured from the pattern are listed in Table 1. XRD spectra of Zr₃N₄ and ZrN films are shown in Fig. 2e. In the case of Zr₃N₄, two distinct XRD spectra, characteristic of orthorhombic and cubic crystal structures, were obtained, whereas the ZrN films exhibited the typical NaCl cubic structure (referred to as δ-ZrN). The comparison of the measured and calculated XRD peak positions of the c-Zr₃N₄ phase are given in Table 1. The XRD spectra and peak positions of the orthorhombic Zr₃N₄ and ZrN films match well with other reports in the literature³⁰. Although no experimental XRD spectrum for c-Zr₃N₄ is available for comparison, we have calculated the XRD spectrum based on the experimental data of Zerr et al.¹² and theoretical calculations by others¹⁶. It can be seen from Table 1 that our measured electron-diffraction spacings and XRD peak positions for c-Zr₃N₄ films match well with the calculated values, indicating that we have been successful in depositing the phase as a thin film. The slight deviations between the experimental and calculated lattice parameters in Table 1 are attributed to displacement of atoms due to ion bombardment during growth. That is, the creation of vacancies and interstitials during energetic condensation of the impinging ions is probably responsible for the variation in atomic positions in the lattice of our c-Zr₃N₄ thin films.

In addition to the diffraction data, we have also confirmed the deposition of the c-Zr₃N₄ phase through Raman spectroscopy. The Th₃P₄ structure of Zr₃N₄ contains 14 atoms in its unit cell and has T₄ point group. The group theory analysis yields the following...
We have found that the Zr$_3$N$_4$ thin films undergo orthorhombic to cubic phase transformation at optimum ion energy and temperature. We have carried out highly tetrahedral amorphous carbon phase through deposition and thus indicate that the c-Zr$_3$N$_4$ phase is transparent.

Figure 4: Milling test results from uncoated, TiN and c-Zr$_3$N$_4$-coated three flute end mills. The cutting speed was 200 m min$^{-1}$ and the feed rate was 10 m min$^{-1}$. The depth of cut was approximately 1.5–2.0 mm. Standard coolant was used during machining. The milling test was stopped after 250 m. The film thickness for both FCA TiN and c-Zr$_3$N$_4$ was kept constant at 1.2 nm. Uniform coating on the end mill was achieved by rotating the end mills during deposition. The inset shows the wear after milling various lengths of the low carbon steel.

The Zr-N thin films were deposited using filtered cathodic arc apparatus (duct diameter = 12 cm). The base pressure achieved before all depositions was 2 × 10$^{-7}$ torr. The magnetic field used to guide the plasma around the 90° bend was 30 mT esla. A high purity (99.6%), cylindrical cathode (diameter = 6.25 cm, height = 5 cm) was used as the plasma source. The cathode was powered by a direct current arc welding power supply. The arc was ignited by touching an earthed anode (Mo rod with a diameter of 3 mm) to the cathode. The nitrogen in the unmodified FCA depositions was introduced near the cathode. In the modified FCA case, the nitrogen was introduced through a stable nitrogen source.

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**Methods**

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A mm hole in the Zr cathode. The complete poisoning of the cathode surface was found to occur at a pressure of $4 \times 10^{-10}$ Torr. At this pressure, virtually all the nitrogen consumed by the cathode so that no molecular nitrogen could be detected by our Hiden EQP plasma analyser. In this study, all depositions were carried out at an arc current of 75 A and voltage of 19 V. The ion flux at the cathode was kept constant at 4.7 mC cm$^{-2}$ to obtain a deposition rate of $2 \text{ nm} \text{s}^{-1}$. The substrate temperature was adjusted to 400 °C before deposition using a resistive heater and monitored by a thermocouple. The ion energy was controlled by applying a bias voltage using an Advanced Energy 3kW MDX generator. The approximate total ion energy was obtained by adding the initial energy of the ions plus the applied bias. The thicker films were deposited using the two-step process$^2$ where the first step is the creation of an interface layer through ion bombardment at $-1,000 \text{ eV}$ (current density $= 4.5 \text{ mC cm}^{-2}$ for 30 seconds). Subsequent to the ion bombardment, the bias voltage was reduced to $-100 \text{ V}$ to deposit the c-Zr$_3$N$_4$ phase. The creation of the interfacial layer through the initial high-energy bombardment seems to provide suitable adhesion of the highly stressed films to the substrate, although direct measurement of the adhesion is still underway.

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References


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COMPETING FINANCIAL INTERESTS

The authors declare that they have no competing financial interests.