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Full Length Article

Friction and wear behavior of nitrogen-doped ZnO thin films deposited *via* MOCVD under dry contact

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ABSTRACT

Most researches on doped ZnO thin films are tilted toward their applications in optoelectronics and semiconductor devices. Research on their tribological properties is still unfolding. In this work, nitrogen-doped ZnO thin films were deposited on 304 L stainless steel substrate from a combination of zinc acetate and ammonium acetate precursor by MOCVD technique. Compositional and structural studies of the films were done using Rutherford Backscattering Spectroscopy (RBS) and X-ray Diffraction (XRD). The frictional behavior of the thin film coatings was evaluated using a ball-on-flat configuration in reciprocating sliding under dry contact condition. After friction test, the flat and ball counter-face surfaces were examined to assess the wear dimension and failure mechanism. Both friction behavior and wear (in the ball counter-face) were observed to be dependent on the crystallinity and thickness of the thin film coatings.

1. Introduction

Over the years, there has been high demand for friction and wear control in all aspects of science and technology. This is because of the enormous amount of energy that is being lost in various systems. In addition, friction and wear reduction do not only bring about energy saving and efficiency, they also increase reliability and durability, which ultimately bring about customer satisfaction.

There are many approaches that have been used in reducing friction and wear. The application of lubricants between moving surfaces to partially or fully separate the contacting surfaces, which then allows for easier movement, is the most common approach. Since failure of engineering materials through friction, wear and fatigue often takes place on the surface of the material, modifying the material surface usually plays important role in reducing friction and wear. Techniques employed in surface modification include, but not limited to, carburization [1,2], plasma nitriding [3,4], ion implantation [5,6], surface texturing [7,8], laser surface modification [9] and thin film coatings [10–12].

Varieties of thin film coatings exist, and there is normally a suitable coating for a given engineering application. In tribological application, the coatings need to posses low shear strength so as to carry the pressure generated between opposing surfaces, thus allowing easier sliding. A large variety of coatings that meet this restriction have been developed, and these can be grouped as soft metal coatings, transition metal dichalcogenide coatings, carbon-based coatings, oxide coatings, sulfate coatings, and polymer coatings, among others.

Until recently, most researches on doped ZnO thin films were more about their applications in UV-light emitters, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers and so on. However, research on the tribological properties of doped ZnO is still evolving. The open structure and favorable coordination number of ZnO could allow for accommodation of external atoms as zinc or oxygen substitutes. This permits the formation of defects through doping, which can cause the formation of slip systems that can alter the electronic structure and lower the shear strength. Thin film coatings of alumina doped ZnO have been shown to have low friction coefficient and better wear performance than pure ZnO thin film coatings [13]. Furthermore, compositing ZnO with organic polymer such as nylon and polyimide has also been shown to improve tribological performance [14–17].

In this work, nitrogen-doped ZnO thin films were deposited on 304 L stainless steel substrate from different combinations of zinc acetate and ammonium acetate precursor using metal organic chemical vapor deposition (MOCVD) technique. Compositional and

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Table 1
Various combinations of precursor used for the deposition of the thin films.

Coating	Precursor combination
A0	100% zinc acetate
A1	90% zinc acetate and 10% ammonium acetate
A2	80% zinc acetate and 20% ammonium acetate
A3	70% zinc acetate and 30% ammonium acetate
A4	60% zinc acetate and 40% ammonium acetate

structural studies of the films were done using Rutherford backscattering spectroscopy (RBS) and X-ray diffraction (XRD). The frictional behavior of the thin film coatings was evaluated using a ball-on-flat configuration in reciprocating sliding with the aid of a high frequency reciprocating rig (HFRR) under dry contact condition. After friction test, the flat and ball counter-face surfaces were also examined to assess the wear dimension and failure mechanism.

2. Materials and methods

2.1. Film deposition

The thin film coatings were deposited on 304 L stainless steel using the pyrolytic method of MOCVD technique. The precursor used was a combination of zinc acetate and ammonium acetate in different proportions. Five sets of coatings were produced at deposition temperature of 420 °C and gas flow rate of 2.5 dm^3/min for 2-hour deposition time using different proportions of zinc acetate and ammonium acetate. The coatings were designated as A0, A1, A2, A3 and A4 for easy identification. Table 1 shows the various combination of the precursor used. Coating A0 serves as a form of control for the other coatings since pure zinc acetate was used as the precursor.

2.2. Thin film characterization

Rutherford backscattering spectroscopy (RBS) was used to determine the stoichiometry and thickness of the thin film coatings. The RBS facility is a 1.7 MeV tandem accelerator of IBM geometry, that is, scattering configuration where the incident beam, surface normal, and detected beam are all coplanar. The incident beam was He$^+$ with beam current of 3.8 nA. SIMNRA software was used to analyze the spectrum that was extracted from the silicon detector of the RBS facility.

The crystal structure of the thin film coatings was determined using MD-10 mini diffractometer. A Cu-K$_\alpha$ radiation was used as the source of radiation. The applied voltage was 25 kV for an exposure time of 1200 seconds. Chemical phase identification was performed using a computer-based system with powder diffraction file (PDF) embedded in it. A database from the International Center for Diffraction was also used in comparing the XRD pattern of the films. The intensity data were collected over a 2θ range of 15°–50°.

2.3. Friction and wear test

Friction test was conducted with a ball-on-flat configuration in reciprocating sliding using a high frequency reciprocating rig (HFRR). Fig. 1 shows the schematic diagram of contact configuration of the HFRR used. The ball counter-face specimen was Al alloy 2017 with a diameter of 12.7 mm. The ball hardness is 1.2 GPa (66 R$_B$) with elastic modulus (E) of 72.4 GPa and Poisson's ratio (ν) of 0.3. Six samples of flat were tested – the uncoated substrate with isotropic finish similar to the coatings (baseline) and the substrates coated with thin films using the various precursor combinations as listed in Table 1. The surface properties of the coatings have been reported earlier [18]; however, Table 2 shows the 2-D roughness data (R$_a$) of the coatings.

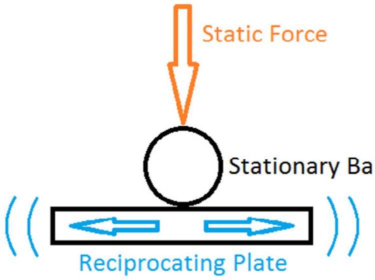

Fig. 1. Schematic diagram of reciprocating ball-on-flat contact.

For each test, flat and ball specimens were mounted on their respective holders and fixed to the test rig. The load was initiated by applying dead weight of 10 N, which imposes a nominal Hertzian contact pressure of 0.35 GPa, while the stroke length was set to 20 mm. The reciprocating speed was 60 rpm for a test time of ten minutes.

Frictional force (F) was continuously monitored for the entire duration of each test. A computer data acquisition system was used to record sliding friction force (F) at relatively high acquisition rate. The coefficient of friction (μ) defined as the ratio of the frictional force (F) to the normal force (N) was then calculated.

At the conclusion of each test, wear dimensions on ball and flat samples were measured by optical microscope and optical profilometer respectively. Worn surfaces were also examined to assess the wear mechanisms.

3. Results and discussion

3.1. Compositional study and thickness analysis

The compositional study and thickness analysis were carried out by RBS. The RBS spectrum of the control coating (A0) is shown in Fig. 2(a). The expected elements zinc and oxygen were detected, with zinc to oxygen ratio of 1:1. This ratio is consistent with elemental composition of pure crystalline ZnO. The RBS spectra of the other coatings from various combination of zinc acetate and ammonium acetate precursor were all similar. Fig. 2(b) shows a typical spectrum of the nitrogen-doped ZnO. The presence of Zn, O and N is clearly manifested. Both spectra depict two distinct sections, the substrate section and the coating section centered around 1450 keV energy. The simulated spectrum is based on hypothetical data in the database of the analyzing software for the elements envisaged. Then based on the simulated spectrum, the read data from the sample are characterized. Each element detected is matched with the database for identification, while the overall concentration of the detected elements gives rise to the thickness of the thin film.

The stoichiometry of the doped zinc oxide coatings exhibited no particular trend with respect to the proportion of zinc acetate and ammonium acetate in the precursor. Each doped zinc oxide coating gave an approximately consistent Zn:O:N ratio of 5:4:1, irrespective of the percentage of ammonium acetate (providing the nitrogen) in the prevailing precursor. Mbamara et al. (2012) [19] had

Table 2
2D roughness data (R$_a$) of coatings.

Coatings	Roughness R$_a$ (nm)
A0	200.91
A1	203.95
A2	164.14
A3	145.76
A4	121.93