Original Research Article

Effect of Deposition Temperature on the Tribology of MOCVD Zinc Oxide Thin Films Testedunder Dry Contact

Abstract

Zinc oxide has justifiably been attracting attention in several fields, and the relatively new field of tribology is not left out. Aside from its already extensively researched and documented applications in materials science, semiconductor and electronics industry, zinc oxide nanoparticles and thin films appear to begaining fast grounds as tribological materials, thereby justifying a zealous approach in further exploring their inherent properties in this area. In this work, zinc oxide thin films were deposited by MOCVD (metal-organic chemical vapour deposition) on soda lime glass and AISI304L stainless steel platesat temperatures of 300°C, 330°C, 360°C, 390°C and 420°C respectively, using anhydrous zinc acetate as the precursor. The carrier gas was air with a flow rate of 2.5 dm^3min^{-1} at atmospheric pressure, and deposition time of 2 hours each.Thethickness and tribologicalproperties of the thin films produced were thereafter investigated. The thickness was measured by RBS (Rutherford backscattering spectroscopy) using a 1.7 MeV Tandem Accelerator, and the friction and wear properties were tested with a HFRR (high frequency reciprocating rig) under dry contact conditions,Olympus BH-2 Optical Microscope, andADE Phase Shift MicroXam Optical Surface Profiler.The thickness was found to decrease with increasing deposition temperature, although for the 300°C deposition temperature there appeared to be a bloated thickness, which is attributable to such factors as incomplete precursor decomposition, turbulence in precursor flow, and energy straggling during RBS measurement. The friction tests highlighted coefficients of friction which were relatively low at the onset of the tests, but thereafter rapidly increased, owing possibly to temperature rise, attendant rapid oxidation and aided abrasion by worn debris. The average coefficient of friction of each test was computed, and the outcome (0.33 – 0.43) for all of them was a material still good enough for use in reducing friction at nanolevel, even with worn out matter and increased working temperature, with no noticeable trend regarding their varied deposition temperatures.Microscope and profilometer profiles vividly showed wear scars with material removal and material transfer. The average wear scar diameters as well as the wear volumeswerecompiledfor both the test balls and the thin films. The result showed a largely correlated trend in the wear scar diameters and the wear volumes, and the thin film deposited at 330°C was the coating with the least wear scars, material removal cum transfer on the test ball and sample. This result is attributed to the enhanced thickness of the sample over the others, apart from sample X1 earlier reported to have a problem in its thickness. This temperature is therefore recommended as the optimum deposition temperature for the best tribologically applicable zinc oxide thin films, using zinc acetate precursor by MOCVD.

Keywords: Zinc oxide;MOCVD; deposition temperature; film thickness;tribology; dry contact.

1 Introduction

Tribology embodies the sub-fields of friction, wear and lubrication. Obviously tribological phenomena have existed right from history, but the formal emergence of the subject as a field of study has elucidated an active and rapidly expanding area of research. Tribology at micro- and nano-levels is largely silent and unexplored comparably, and so research at those levels demand anunhindered approach from all angles.This is becausethe outcome of most natural and artificial phenomenamajorly emanate from tribology at such levels [1].

Fortunately in recent time, the tribology of thin films and nanoparticles has evoked much interest, and has been quite rapidlyprogressing and yielding tangible dividends in the understanding and harnessing of the subject matter [2]. Much ground is still needed to be covered, however, as unexplored domains are believed to still be much greater than investigated domains [3].

The MOCVD technique offers itself as a veritable tool for the growth of thin films and nanoparticles of various materials of applicable interest in the field of tribology, of which such properties can be explored and put into appropriate use. A material of curious interest here is zinc oxide, which we have here grown by the MOCVD technique, and its tribological properties investigated vis-à-vis the deposition temperature.

The increasing interest in zinc oxide is justified because of its environmental friendliness and renowned versatility. Curiosity about its tribological applications is now trendy. A more tribologically relevant zinc oxide thin film would make for cheap protection of mechanical parts with the environmentally friendly (zinc oxide) material, by using it as a tribo-coating of sensitive and expensive parts. The raw material would be handy and cheap; the process would be easily replicable; and the spent debris would be non-hazardous to dispose of. A few available tribologicalruns with zinc oxide thin films deposited by some alterative deposition techniques have already given promising tribological results [4, 5]. This is a viable impetus for the present interest in the tribology of MOCVD zinc oxide thin films.In the present work, the tribological properties ofzinc oxide thin films deposited by MOCVD at different deposition temperatures using zinc acetate as the precursor, were investigated under dry contact environment.

2Materials and Method

10 g of anhydrous zinc acetate, $Zn(O_2CCH_3)_2$, which is the precursor was introduced into the receptacle of an MOCVD set up for each deposition process, using five temperatures – 300°C, 330°C, 360°C, 390°C and 420°C – as the deposition temperatures. Air was used as the carrier gas for the precursor with a flow rate of 2.5 dm^3min^{-1}, and each deposition was carried out for 2 hours at atmospheric pressure. Both soda lime glass and AISI304L stainless steel plates were used as substrates for eachdeposition. The thin films realized at the different temperatures were subsequently labelled as X1, X2, X3, X4 and X5 respectively.

The thin films were subjected to characterization by Rutherford backscattering spectroscopy (RBS), Optical microscopy, Optical profilometry and High frequency reciprocating rig (HFRR) tribometry. Samples deposited on glass plates were used for the RBS tests, and samples deposited on stainless steel plates were used for thd rest of the tests. The RBS tests were carried out with a 1.7 MeV Tandem Accelerator to identify the elements present in the samples and also reveal their thicknesses; the optical microscopy was carried out with Olympus BH-2 Optical Microscope; and the profilometry was achieved with ADE Phase Shift MicroXam Optical Surface Profiler.The microscopy and profilometry of the samples were carried out before and after indentation with the HFRR.The profilometry measurements were carried out in both 2 dimensions (2D) and 3 dimensions (3D).

The HFRR was used to measure the friction and wear characteristics of the samples, based on ASTM Specification G 133 on 'Standard Test Method for Linearly Reciprocating Ball-on-flat Sliding Wear Tests'. Al 2017 alloy ball was used as the counter-face indenter, with the following parameters: Diameter – 0.5"; Hardness – 1.2 GPa (or 66 Ra); Elastic modulus (E) – 72.4 GPa; Poisson ratio (ν) – 0.3. The friction between the test balls and the respective flat samples were recorded directly as the tribology tests were on for 10 mins., and the resulting wear volumes were estimated from both the wear scar diameters, and by measuring the ball and sample weights before and after each test. All the tests were implemented under dry contact conditions, andthe weight measurements were carried out after washing and drying the samples.

3 Results and Discussion

3.1 Composition and Thickness Measurements

Figure 1(a) to (e) shows the RBS spectra of the thin films. The key elements, zinc and oxygen, were revealed in the samples, each with an approximate ratio of 1:1. The composition and ratio conform tothatof pure crystalline ZnO thin film. The thin film thicknesses were also recorded for X1, X2, X3, X4 and X5 as 741, 299, 297, 267 and 185 nm respectively.This implies that the thickness of the thin films reduced as the deposition temperature increased.This may be explained as decrease in the nucleation

and crystallization processes as the deposition temperatures increased. The spectrum shown in figure 1(e) and recorded as X0 is for a blank substrate, which is set to act as the control all through.The thickness trendis recorded in Table 1.

From the RBS data the thickness of X1 is abnormally higher than the rest of the deposited thin films. This abnormality is attributable to either or all of three possible causes: its deposition temperature is the lowest (300°C) in the range of deposition temperatures and there could have been incomplete decomposition of the precursor, leading to a thin film from both completely decomposed and incompletely decomposed precursor; there could have been some turbulence during the precursor delivery, leading to the transportation and delivery of an abnormally higher quantity of precursor to the cracking chamber than normal; there could also have been energy straggling during the RBS analysis of this very sample, leading to a bloated thickness [6, 7].

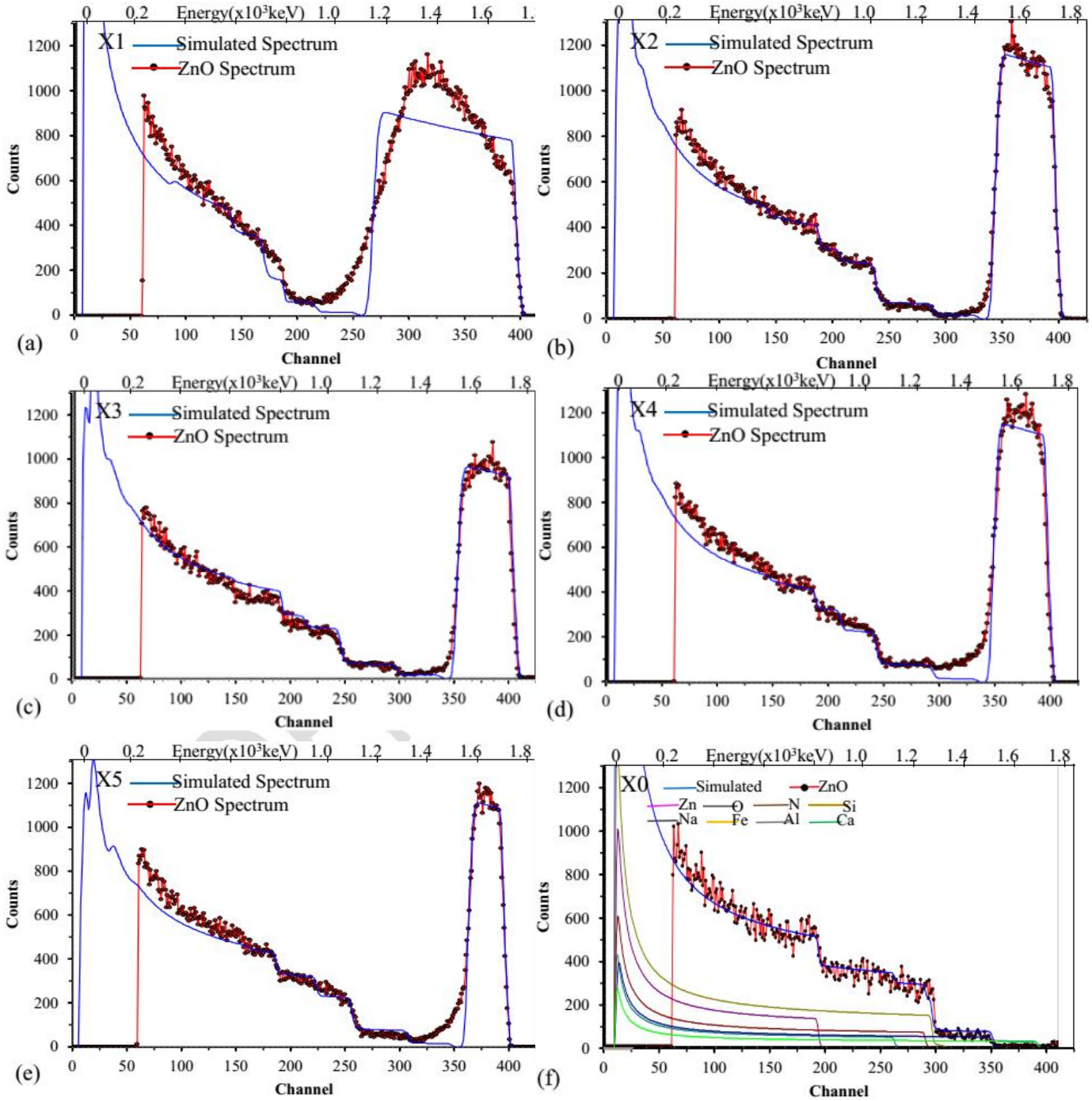


Fig. 1. RBS spectra of the deposited thin films.

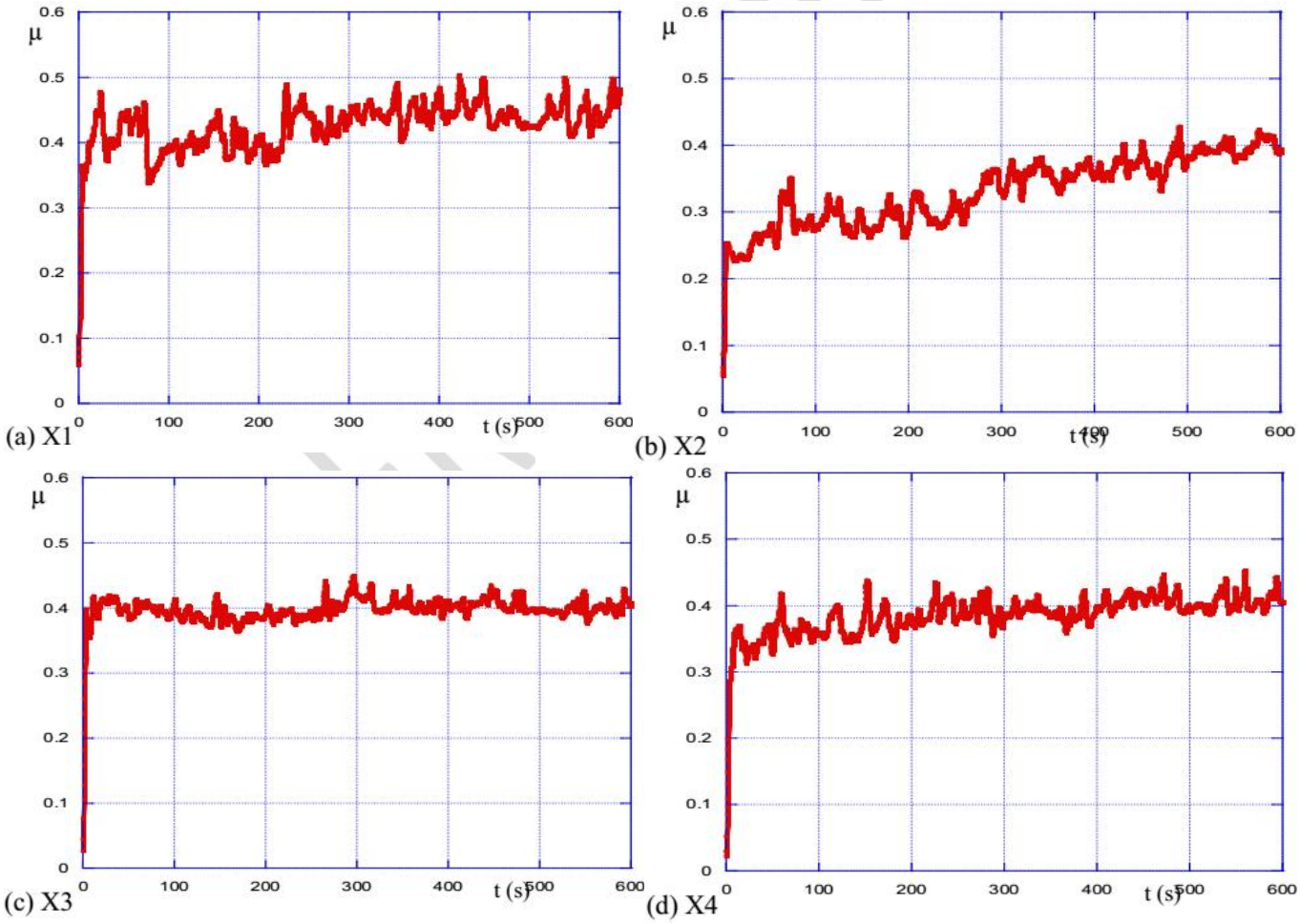
Table 1. Thickness, friction and wear results of the deposited thin films

Sample	Film thickness	Average	Average wear diameter	Wear volume

	(nm)	friction	$Ø_a$ (nm)		(x10^6 µm^3)	
		μ_a	Test ball	Sample	Test ball	Sample
X1	741	0.43	1395	1268	-18.1	116
X2	299	0.33	1316	1026	-8.6	67
X3	297	0.4	1558	1274	-13.9	185
X4	267	0.39	1405	1242	-18.6	120
X5	185	0.4	1621	1232	-16.6	110
X0	0	0.39	1437	1368	-39.1	419

3.2 Friction Measurements

Figure 2 shows the variation of friction with time for an uncoated substrate and for the five coatings.For X1, the coefficient of friction, µ, started at 0.07 and increased rapidly, reaching a maximum of about 0.50; for X2, µ started with a value of 0.05, and then increased with time, ranging between 0.24 and 0.44; for X3, µ started at 0.02 and quickly jumped to 0.40, then hovered between 0.37 and 0.45 to the end; for X4, µ started with a value of 0.02 and increased to a maximum of 0.46 around which it remained till the end; for X5, µ started with a value of 0.06 and increased to 0.47 for the rest of the test; and for the uncoated substrate, X0, µ started with a value of 0.01 and quickly jumped to a value of 0.44, thereafter ranging between 0.36 and 0.46 till the end.As a general trend, the friction values started at very low values and then rapidly transited to much higher values in all the samples, and obviously coinciding with the wearing through of the thin films. From the onset of the tests, initially worn debris may have aided the abrasion of the rest of the coatings through the contact paths, leading to the observed high values for µ in the later part of the tests as the charts in Figure 2 show.



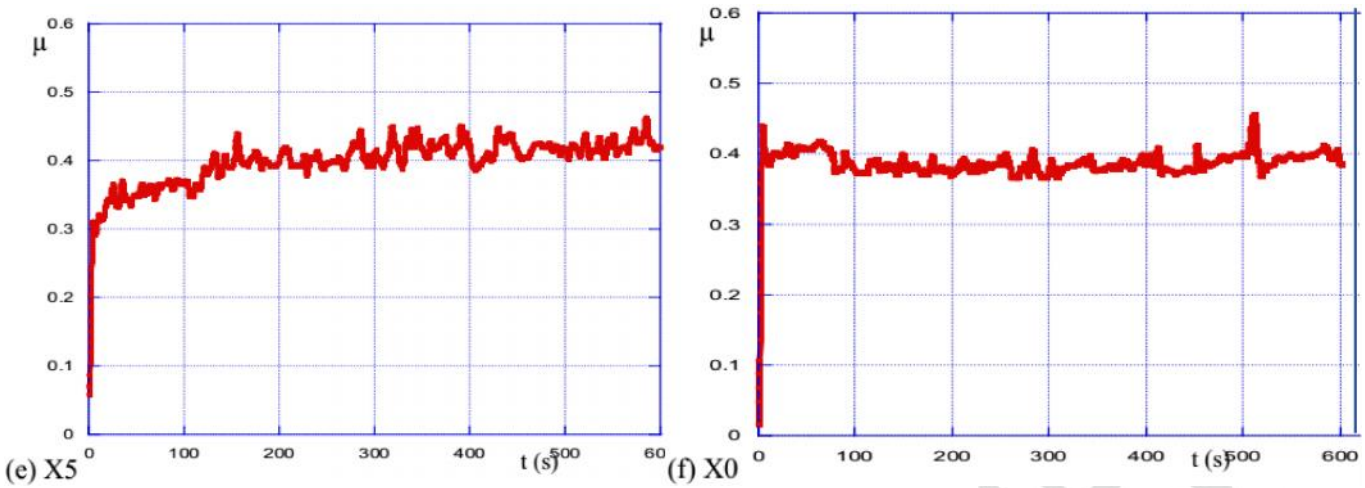
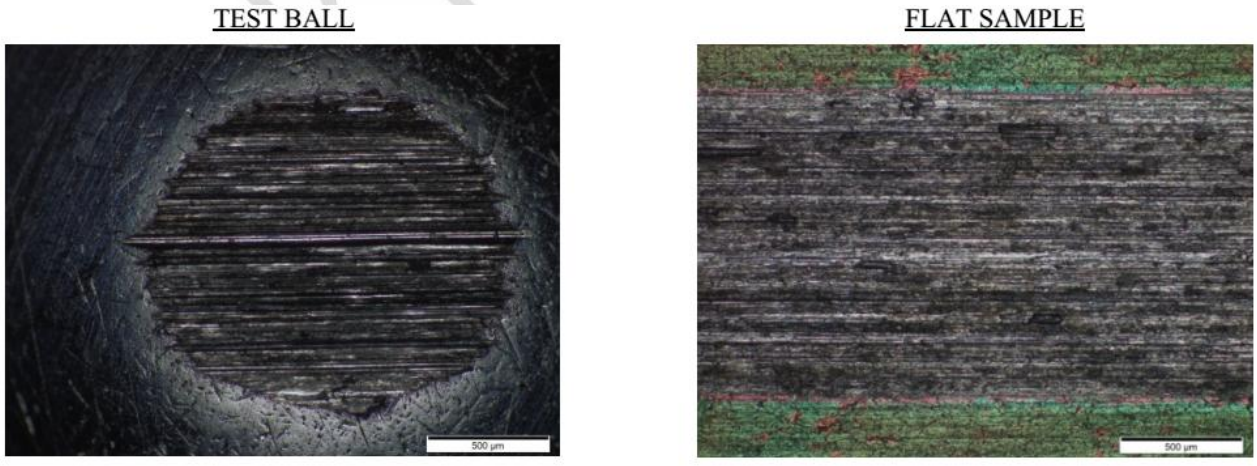


Fig. 2. Friction charts of the thin films.

The average values of the coefficients of friction, μ_a, were also recorded for the samples. The values obtained for μ_a are recorded in Table 1. From the record, the coating on X2 has the lowest average coefficient of friction (μ_a= 0.33) while the coating on X1 has the highest (μ_a= 0.43). μ_a, for the uncoated substrate and the rest of the coatings lie in between these extreme values. On the whole, the values obtained for the average coefficient of friction fairly lie within the limits for good tribological materials, for example, CaF_2 (μ_a = 0.4) and $PbMoO_2$ (μ_a = 0.35-0.4) [8]. In reality, however, the average coefficient of friction does not strictly represent the frictional behaviour of the thin films, due to the action of heat and initially worn materials in aiding oxidation and abrasive wear as the friction tests progressed. The different microstructures and ball surface asperities may have been compromised by those factors, thereby leading to larger tensile stress accumulations which could have adversely affected the adhesion of the thin films to the substrates. The end effects would be somewhat fictitious (bloated) friction and wear values. The coefficients of friction recorded at the onset of each test therefore more realistically reflect the coefficients of friction of the thin films, or nearly so [9], and they portray excellent low friction materials.

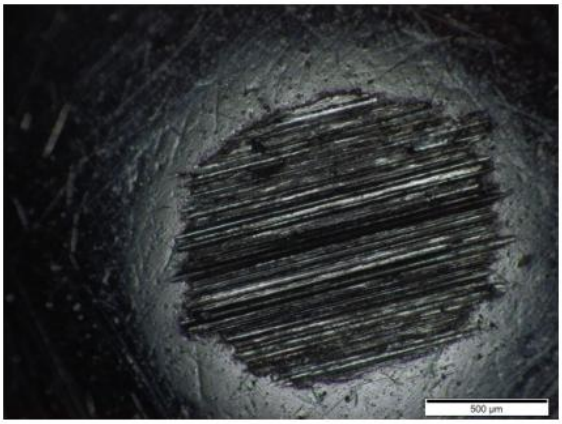
3.3 Wear Scar Measurements

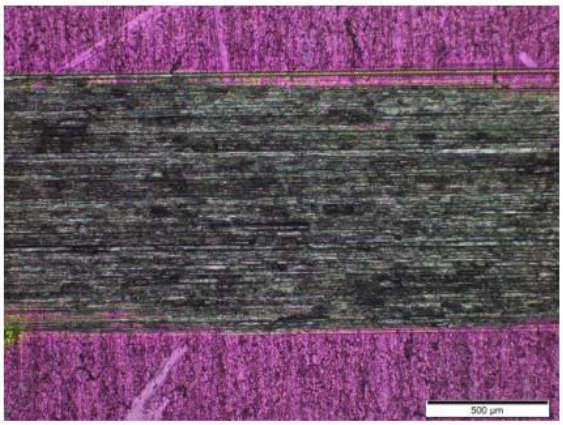
Wear scars in the test balls and the samples were recorded with the optical microscope, as displayed in Figure 3. White bars representing the magnification scales at 50 μm are inset on the lower right of the images. For all the samples X1 to X5, the test balls had abrasive wear while the samples had net material transfer; for the uncoated substrate, there was also abrasive wear on the test ball and evidence of material transfer on the plane substrate. These observations similarly apply to the profilometry images which are presented in Figure 4.



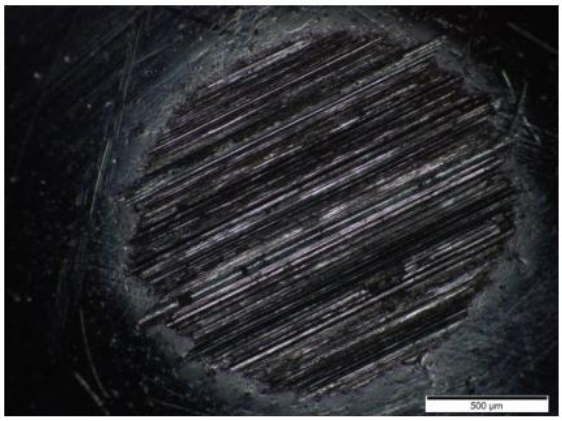
(a) X1

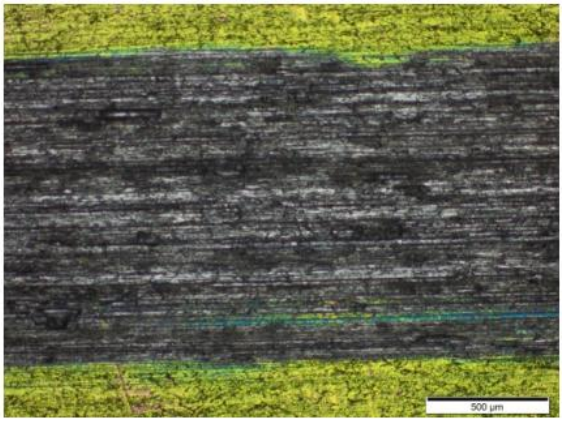
(b) X2



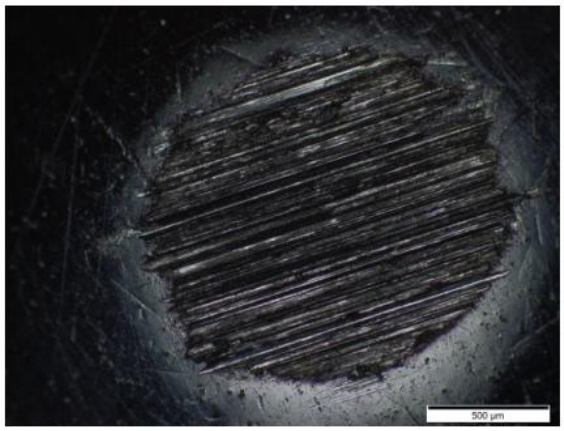


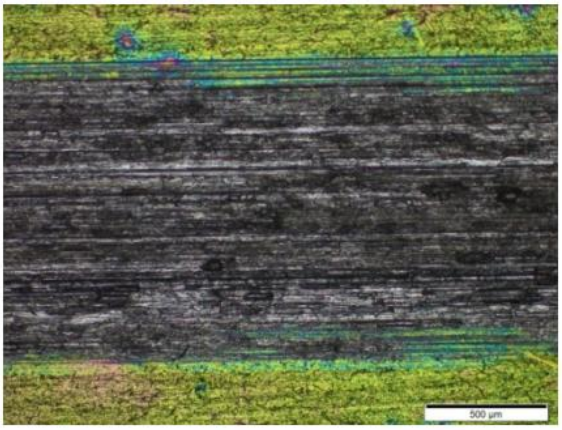
(c) X3

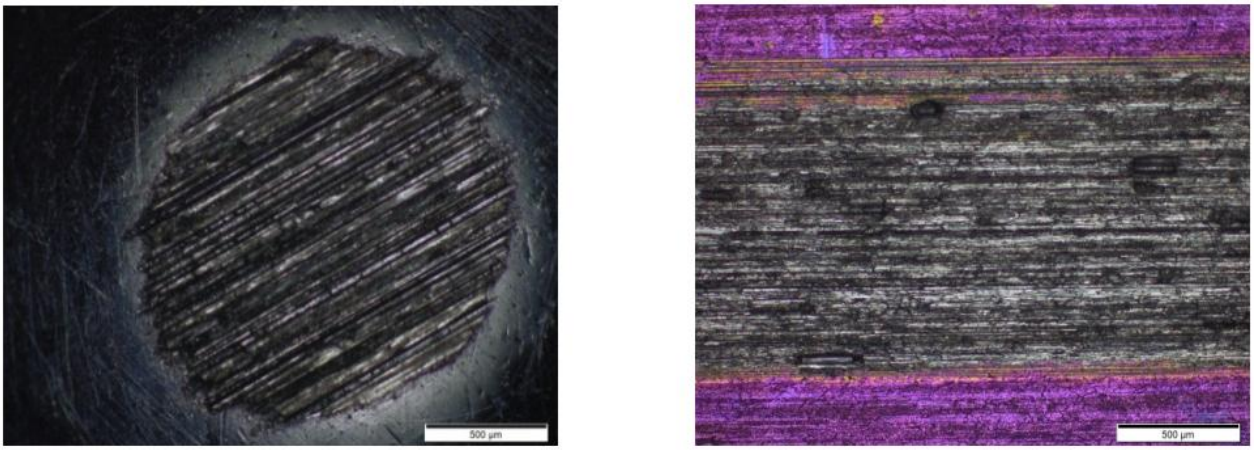




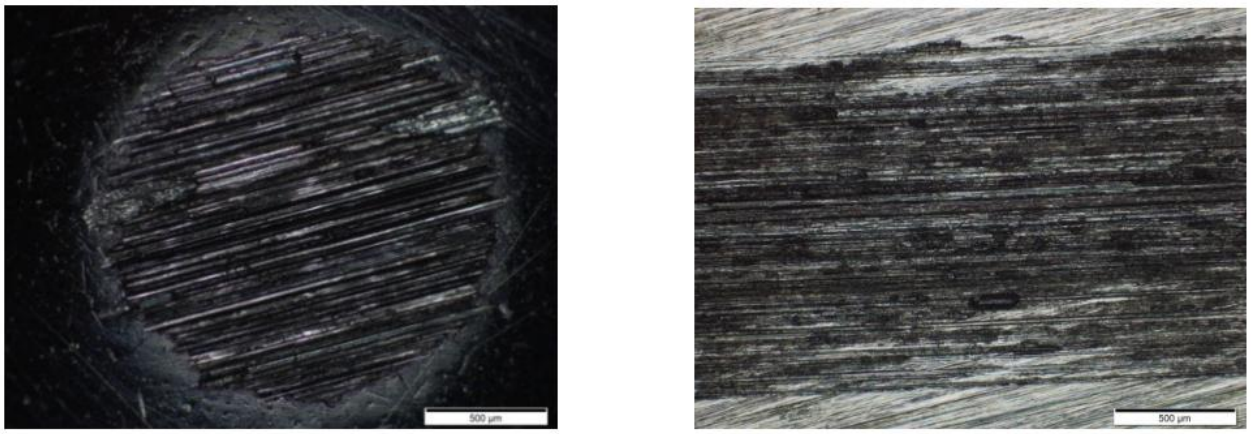
(d) X4







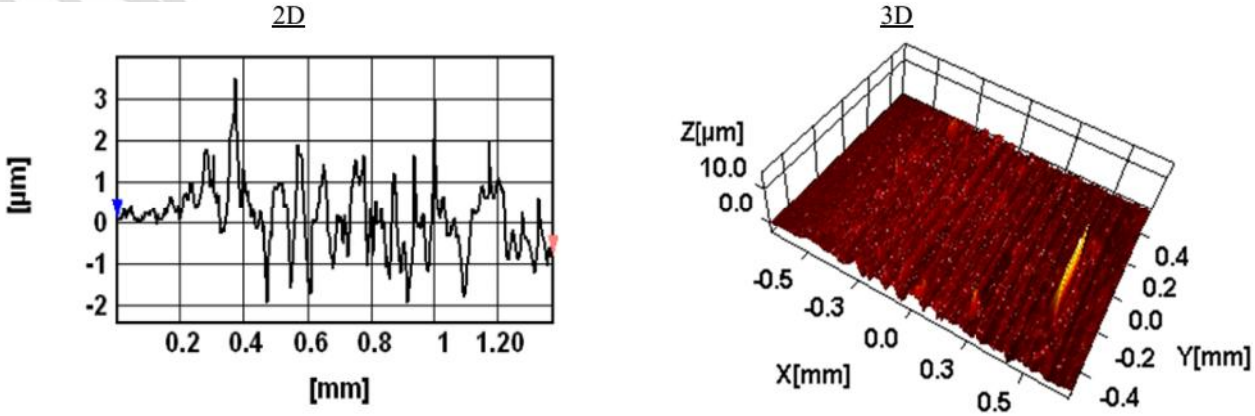
(e) X5



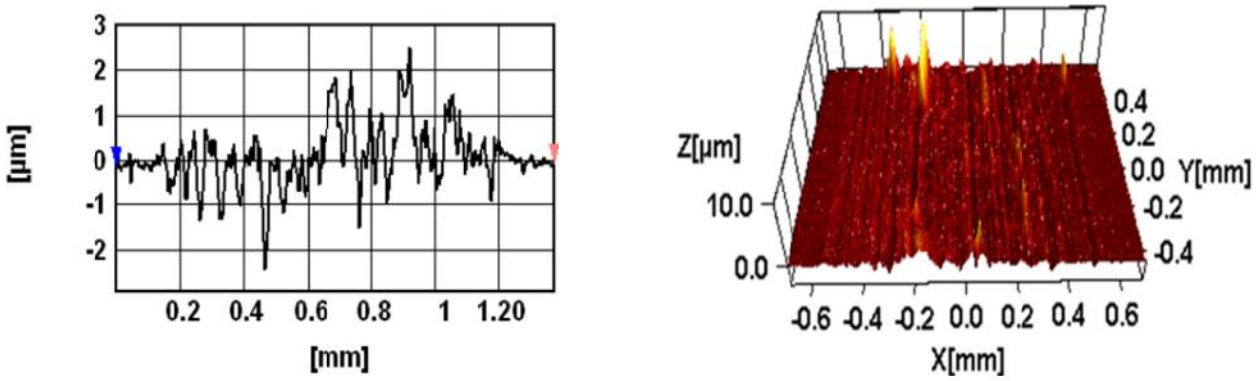
(f) X0

Fig.3. Wear scars on the test balls and sample surfaces.

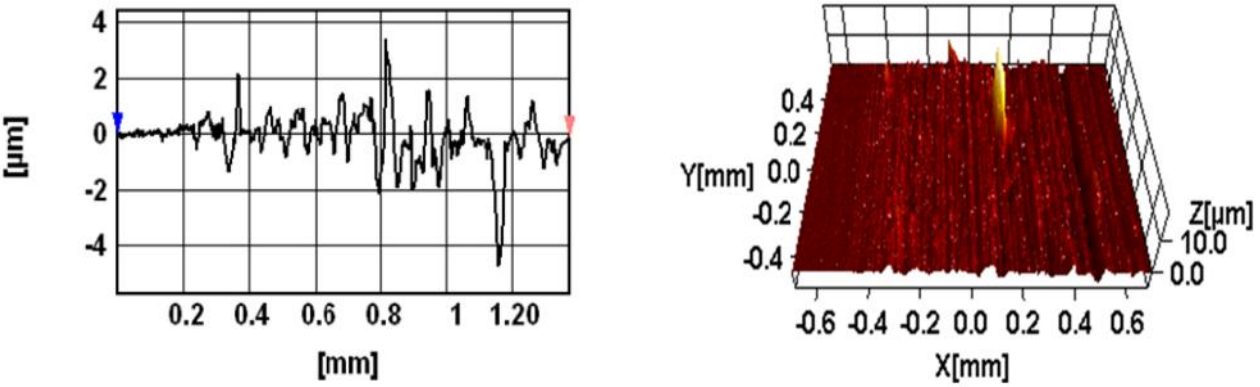
The wear scars on the microscopy images were measured and the average wear scar diameters, $Ø_a$, estimated. For the test ball – sample systems we had: 1395 µm, 1268 µm for X1; 1316 µm, 1026 µm for X2; 1558 µm, 1274 µm for X3; 1405 µm, 1242 µm forX4; 1621 µm, 1232 µm for X5; and 1437 µm, 1368 µm for the uncoated substrate, for the test balls and their flat samples respectively. These results are represented in Table 1. The least wear scar on the test balls was for sample X2 (1316 µm), and the highest on the test balls was for sample X5 (1621 µm); the least wear scar on the flat samples themselves was on sample X2 (1026 µm), and the highest on the samples was on sample X3 (1274 µm); the wear scar on the uncoated substrate, however, is still higher (1368 µm) than that on X3.Aside from the coefficient of friction and the wear volume, the wear scar diameter helps in assessing and comparing the extent of friction and wear on the sets of surfaces, and is also used in calculating the wear volume itself.



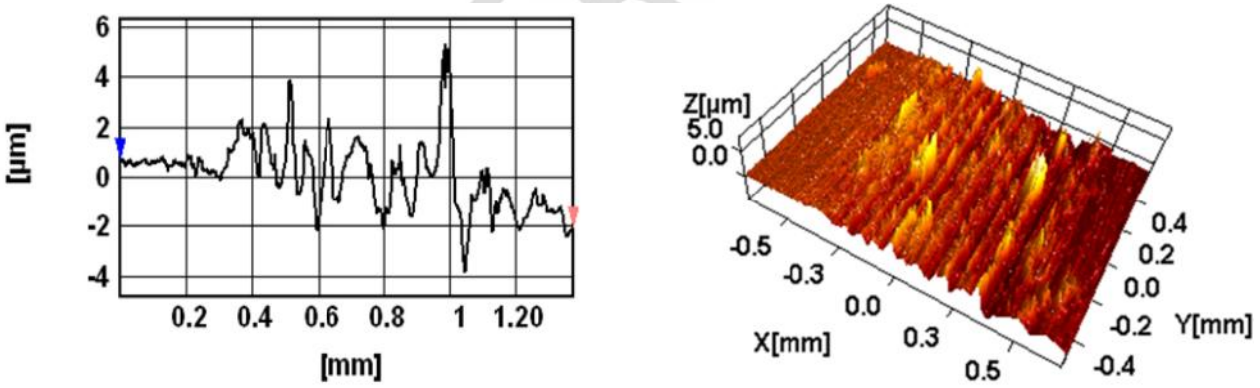
(a) X1



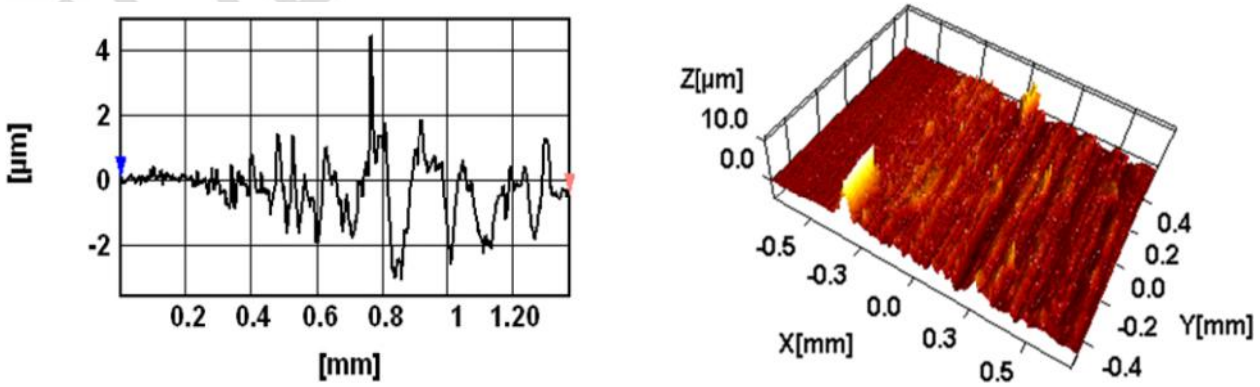
(b) X2



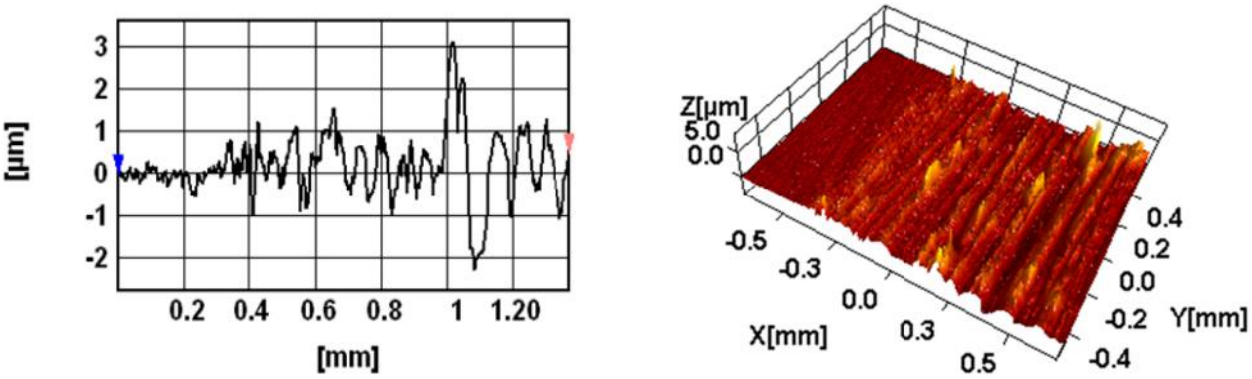
(c) X3



(d) X4



(e) X5



(f) X0

Fig. 4. Surface profiles of the sample surfaces imaged with the profilometer.

3.4 Wear Volume Measurements

The worn images of the thin film samples as captured by the optical profilometry in both 2 dimensions (2D) and 3 dimensions (3D) are shown in Figure 4. In all the wear tests, there was net material transfer from the test balls to the flat surfaces. The wear volumes of all the test ballswere therefore recorded as negative (abrasive), while the wear volumes of all the flat samples (all with material transfers) were recorded as positive (transfer). It should however be noted that in reality there is nothing like 'negative volume'. The optical profilometry was used in estimating the abrasive wear and material transfers. The wear volumes for all the test balls were estimated with the expression [6]:

$$V = \pi d^4/64r \qquad (1)$$

where d = wear scar diameter and r = radius of the ball. The corresponding wear volumes for all the flat samples were estimated from the 2D profilometry measurements. The wear volumes of the test balls and the flat samples are incorporated into Table 1.

From the records, the least wear volume from a test ball was for X2 ($8.6x10^6$ µm^3), and the highest wear volume from a test ball was for X4 ($18.6x10^6$ µm^3); the least wear volume from a flat sample was from X2 ($67x10^6$ µm^3), and the highest wear volume from a flat sample was from X3 ($185x10^6$ µm^3). The values for the uncoated substrate, both for the flat ($419x10^6$ µm^3) and the test ball ($39.1x10^6$ µm^3), wear marginally higher than for the samples and their test balls respectively. This shows that the coated substrates with zinc oxide have tribological advantage over the uncoated one. A correlation of the extreme values of friction, wear scar and wear volume also shows that most of the samples involved in the extreme values respectively correspond in the parameters, while sample X2 showed itself to have the least in all, thereby manifesting itself as the best tribological material of all.

Note once more that for the coated samples, the thickness of X1 is unrealisticallyhigh compared with the other samples. The reason for this situation is already explained in subsection 3.1. But the thickness trend for the rest of the samples look more realistic. The wear result of sample X2 gave the best (least) wear result. This is attributable to its relatively thicker coating than the rest, resulting in its reduced friction and wear values over the others [9]. Its deposition temperature is therefore considered as the most favourable for having a good tribological coating of ZnO.

4Conclusion

Deposition temperature has been proved to have effect on the tribological properties of ZnO thin films. While 300°C did not give a reliable result because of an abnormally 'thick' thin film which it produced, the rest of the deposition temperatures – 300°C, 330°C, 360°C, 390°C and 420°C – gave fairly ordered and realistic results. In all, 330°C deposition temperature gave fairly realistic'thick' film which has an enhanced impact of reducing the friction and wear on it, over otherdeposition temperatures.

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