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3 **Effect of Deposition Temperature on the Tribology of MOCVD**
4 **Zinc Oxide Thin Films Tested under Dry Contact**

5

6 **Abstract**

7 Zinc oxide has justifiably been attracting attention in several fields, and the relatively new field of tribology is not left out.
8 Aside from its already extensively researched and documented applications in materials science, semiconductor and
9 electronics industry, zinc oxide nanoparticles and thin films appear to be gaining a fast ground as tribological materials,
10 thereby justifying a zealous approach in further exploring their inherent properties in this area. In this work, zinc oxide thin
11 films were deposited by MOCVD (metal-organic chemical vapour deposition) on soda lime glass and AISI304L stainless
12 steel plates at temperatures of 300°C, 330°C, 360°C, 390°C and 420°C respectively, using anhydrous zinc acetate as the
13 precursor. The carrier gas was air with a flow rate of 2.5 dm³min⁻¹ at atmospheric pressure, and deposition time of 2 hours
14 each. The thickness and tribological properties of the thin films produced were thereafter investigated. The thickness was
15 measured by RBS (Rutherford backscattering spectroscopy) using a 1.7 MeV Tandem Accelerator, and the friction and wear
16 properties were tested with a HFRR (high frequency reciprocating rig) under dry contact conditions, Olympus BH-2 Optical
17 Microscope, and ADE Phase Shift MicroXam Optical Surface Profiler. The thickness was found to decrease with increasing
18 deposition temperature, although for the 300°C deposition temperature there appeared to be a bloated thickness, which is
19 attributable to such factors as incomplete precursor decomposition, turbulence in precursor flow, and energy straggling
20 during RBS measurement. The friction tests highlighted coefficients of friction which were relatively low at the onset of the
21 tests, but thereafter rapidly increased, owing possibly to temperature rise, attendant rapid oxidation and aided abrasion by
22 worn debris. This was so both for test balls on the HFRR and the thin film surfaces. But the starting values of less than 0.1 for
23 all of them depict an excellent low friction material under dry contact. Average coefficient of friction of each test was also
24 computed, and still the outcome (0.33 – 0.43) for all of them was a material still good enough for use in reducing friction at
25 nanolevel even with worn out matter and increased working temperature, with no noticeable trend regarding their varied
26 deposition temperatures. Microscope and profilometer profiles vividly showed wear scars with material removal and material
27 transfer. The average wear scar diameters as well as the wear volumes were compiled for both the test balls and the thin
28 films. The result showed a largely correlated trend in the wear scar diameters and the wear volumes, and the thin film
29 deposited at 330°C was the coating with the least wear scars material removal cum transfer on the test ball and sample. This
30 result is attributed to the enhanced thickness of the sample over the others, apart from sample X1 earlier suspected to have a
31 problem in its thickness. This temperature is therefore recommended as the optimum deposition temperature for the best
32 tribologically applicable zinc oxide thin films, using zinc acetate precursor by MOCVD.

33 **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 an unhindered approach from all angles. This is because the outcome of most natural and artificial phenomena majorly 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 rapidly progressing 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 tribological runs with zinc oxide thin films deposited by some alternative 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 of zinc oxide thin films deposited by MOCVD at different deposition temperatures using zinc acetate as the precursor, were investigated under dry contact environment.

2 Materials 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 $2.5 \text{ dm}^3 \text{ min}^{-1}$, 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 each deposition. 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 the 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, and the weight measurements were carried out after washing and drying the samples.

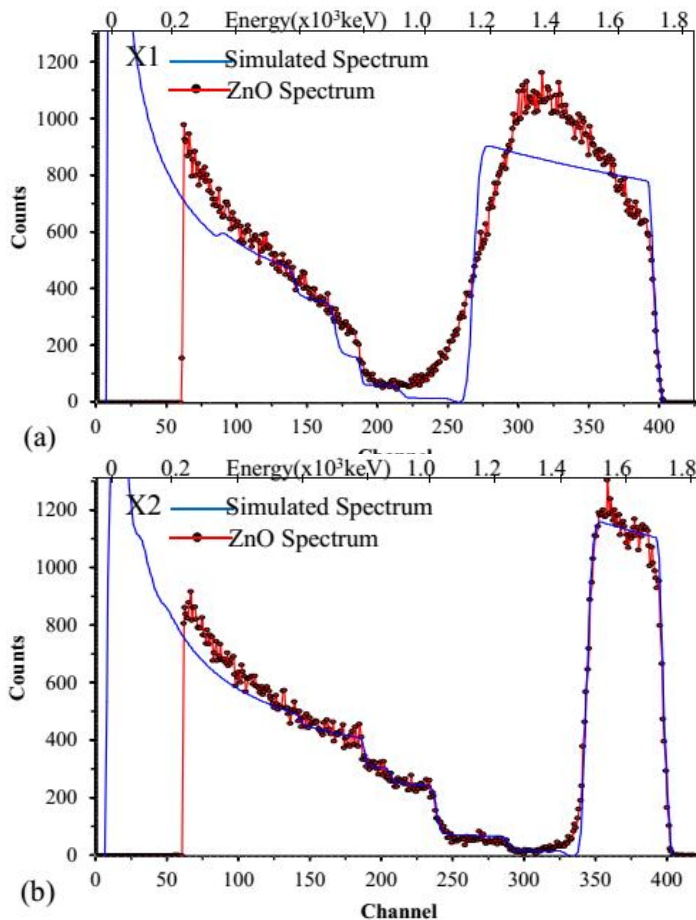
3 Results and Discussion

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 to that of 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 trend is 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].



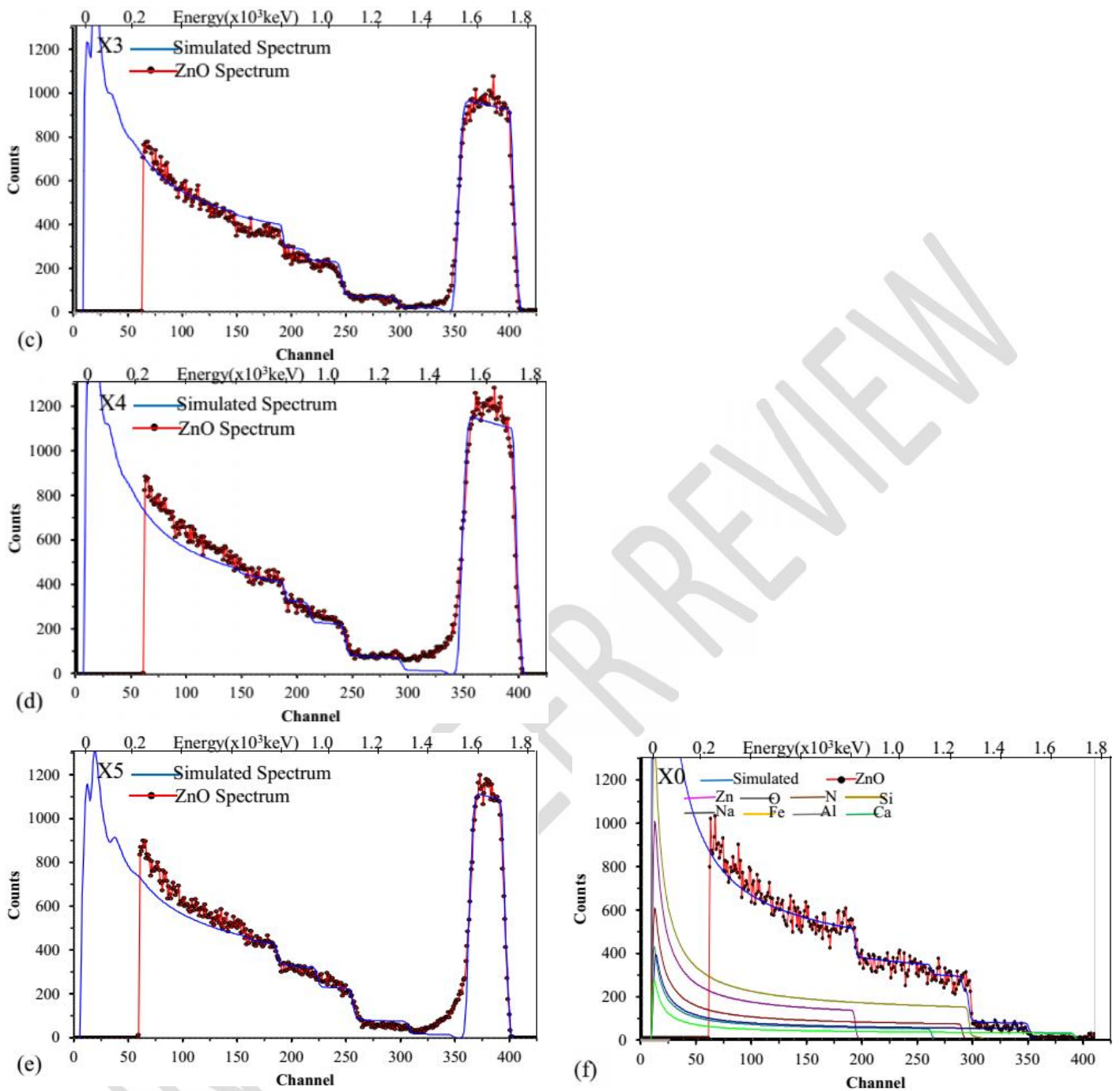


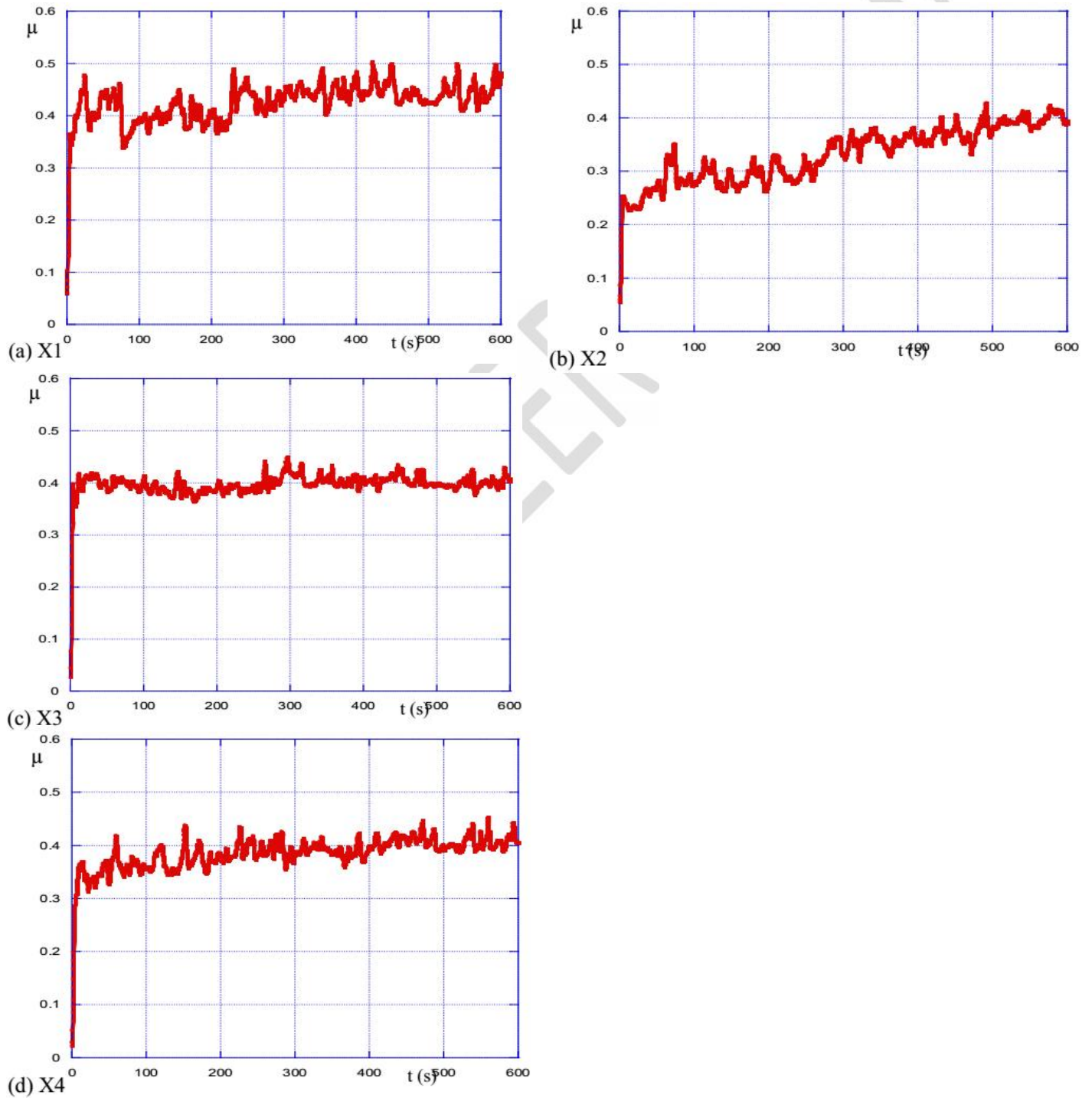
Fig. 1. RBS spectra of the deposited thin films.

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

Sample	Film thickness (nm)	Average friction μ_a	Average wear diameter ϕ_a (nm)		Wear volume ($\times 10^6 \mu m^3$)	
			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.



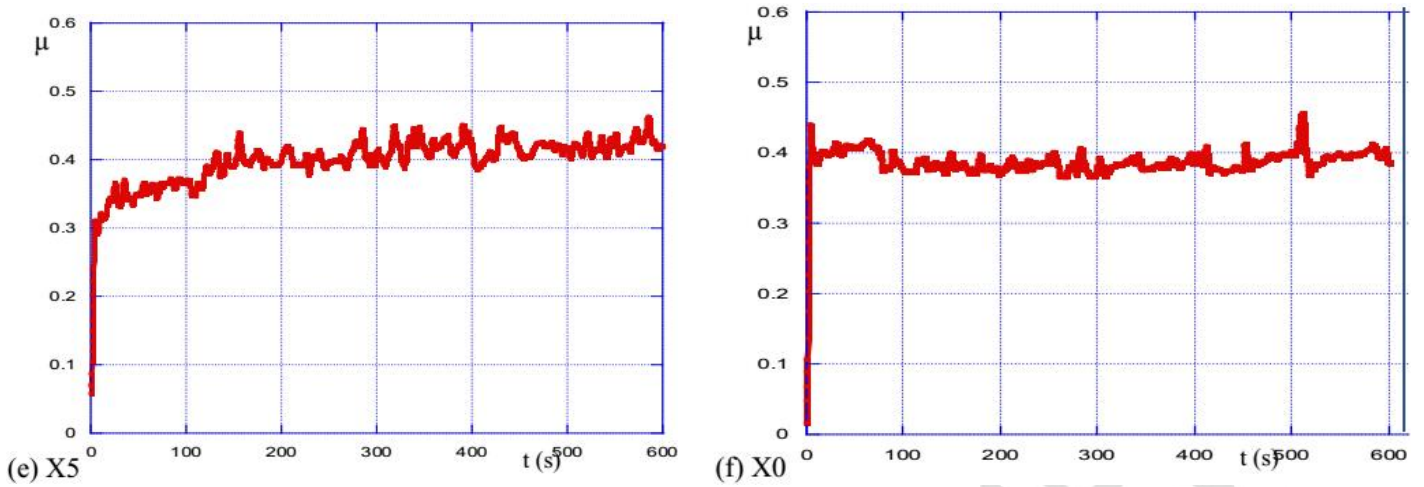
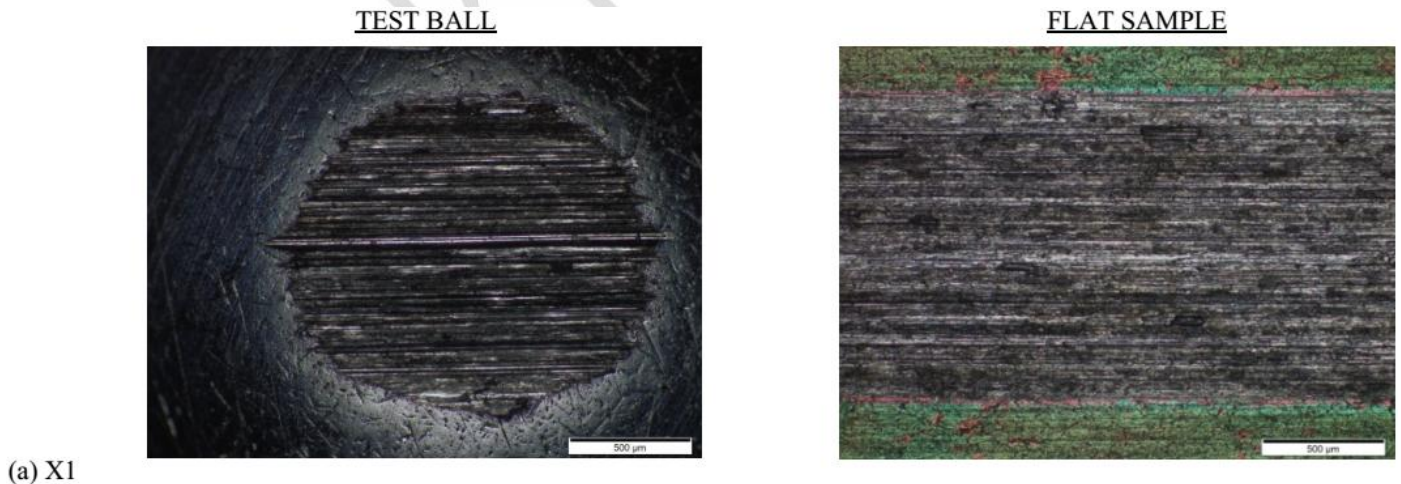


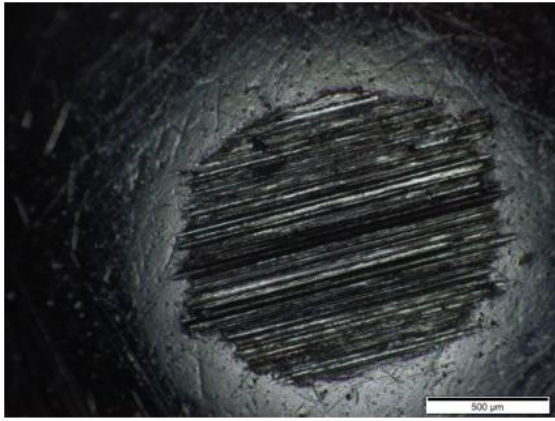
Fig. 2. Friction charts of the thin films.

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 ($\mu_a = 0.33$) while the coating on X1 has the highest ($\mu_a = 0.43$). 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 ($\mu_a = 0.4$) and PbMoO_2 ($\mu_a = 0.35\text{-}0.4$) [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.

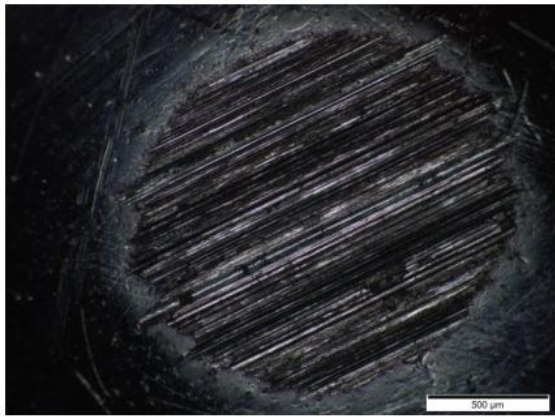
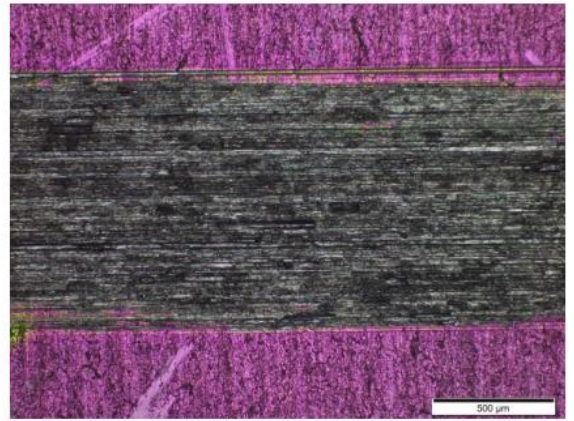
3.3 Wear Scar Measurements

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 $50\ \mu\text{m}$ 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.

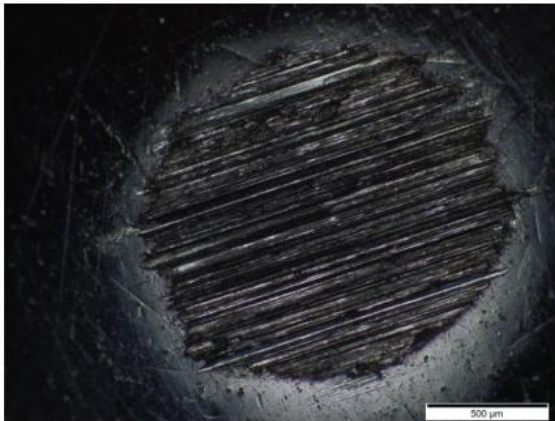
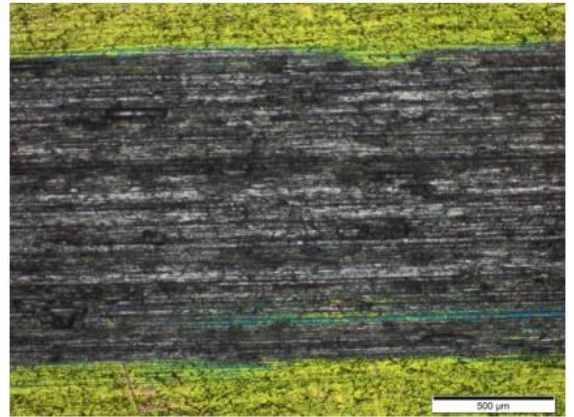




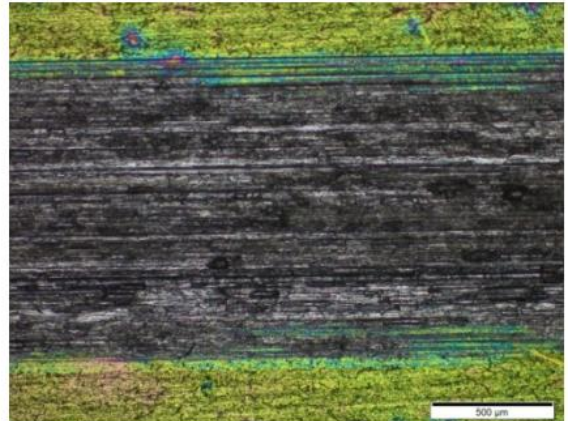
(b) X2

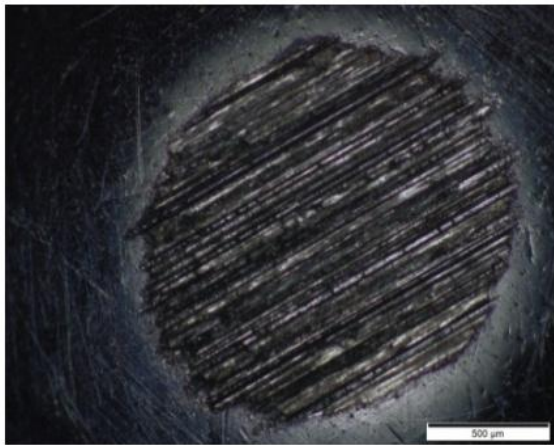


(c) X3

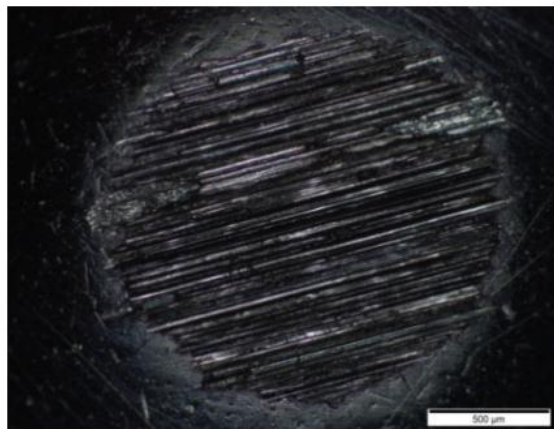
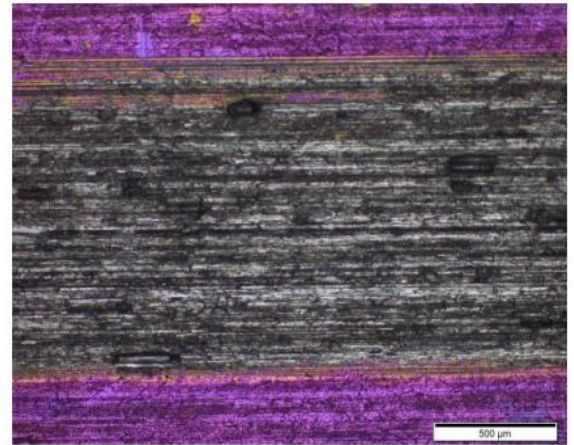


(d) X4





(e) X5



(f) X0

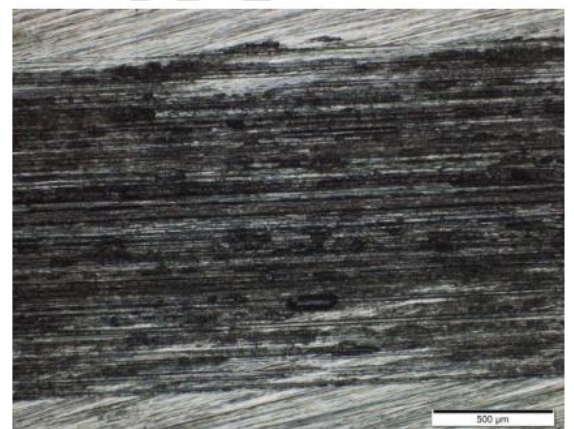
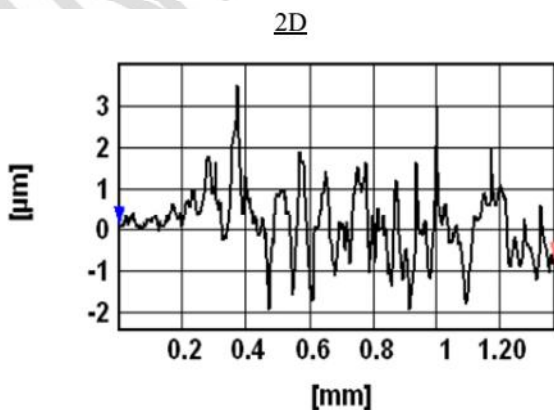
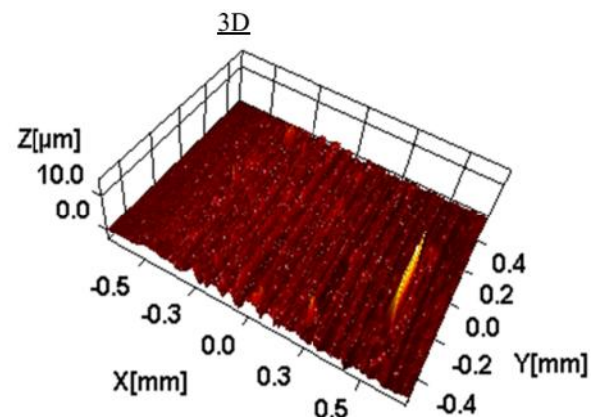


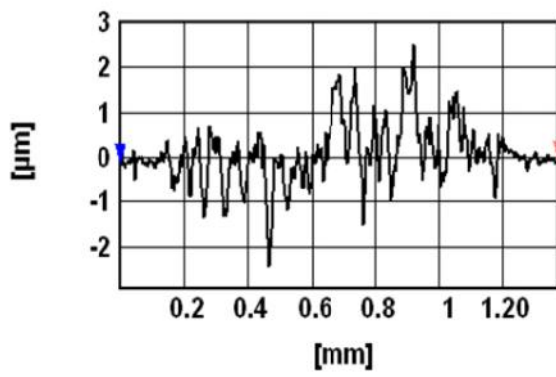
Fig.3. Wear scars on the test balls and sample surfaces.

The wear scars on the microscopy images were measured and the average wear scar diameters, $\bar{\phi}_a$, 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 for X4; 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.

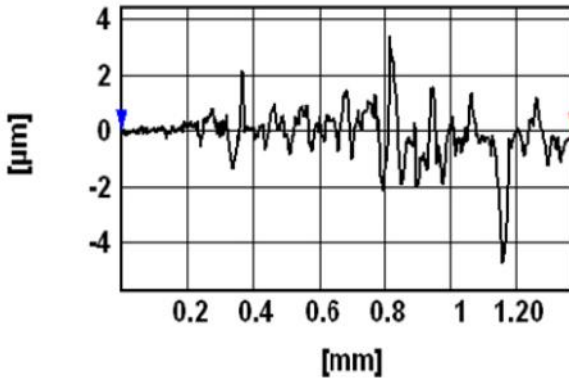
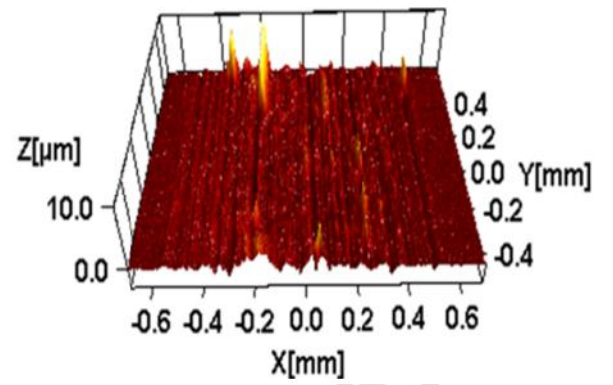


(a) X1

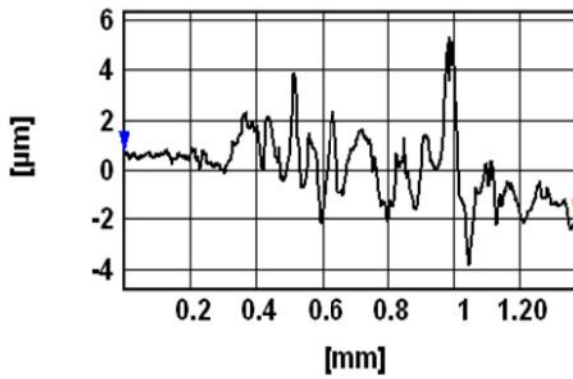
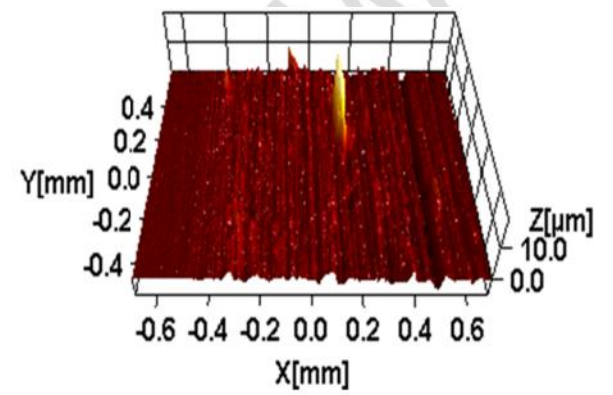




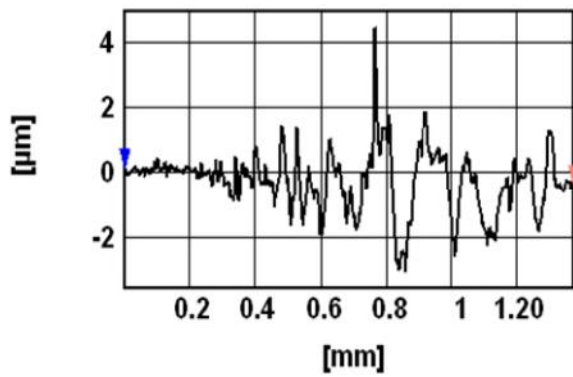
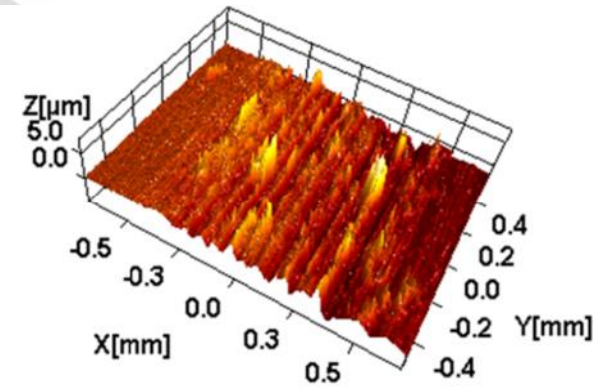
(b) X2



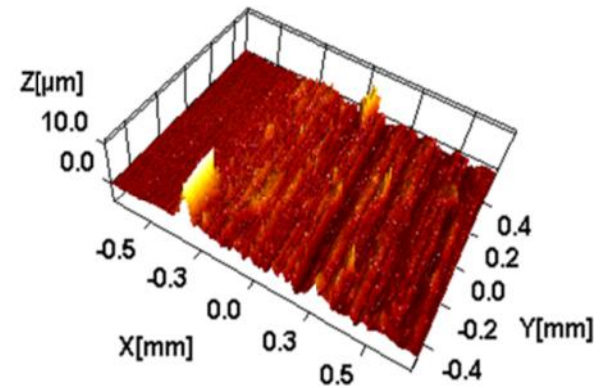
(c) X3

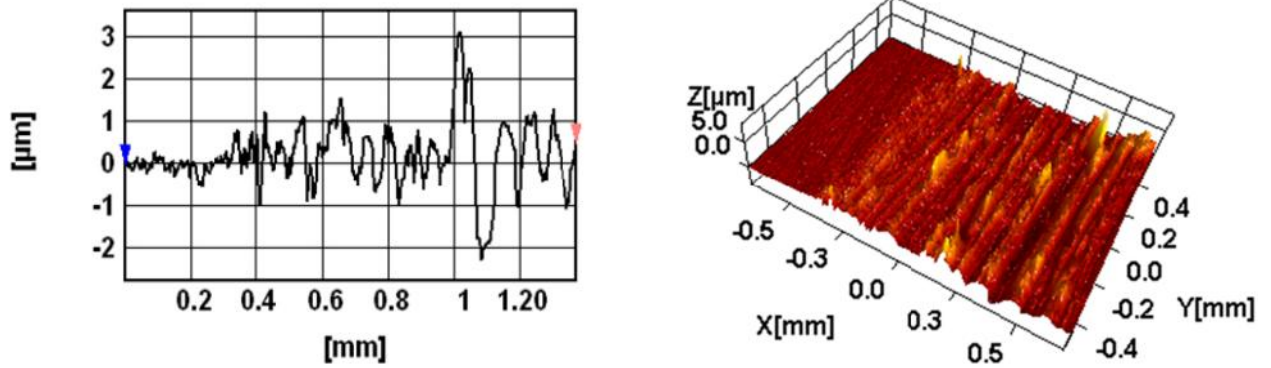


(d) X4



(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 balls were 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]:

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

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 ($8.6 \times 10^6 \mu\text{m}^3$), and the highest wear volume from a test ball was for X4 ($18.6 \times 10^6 \mu\text{m}^3$); the least wear volume from a flat sample was from X2 ($67 \times 10^6 \mu\text{m}^3$), and the highest wear volume from a flat sample was from X3 ($185 \times 10^6 \mu\text{m}^3$). The values for the uncoated substrate, both for the flat ($419 \times 10^6 \mu\text{m}^3$) and the test ball ($39.1 \times 10^6 \mu\text{m}^3$), 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 unrealistically high 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.

4 Conclusion

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 other deposition temperatures.

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