EFFECTS OF NORMAL LOAD ON NANOTRIBOLOGY OF ZINC SULPHIDE (ZnS) AND CADMIUM SULPHIDE (CdS)

Abstract

Energetic losses in systems especially miniaturized systems is presently a global challenge. In this work, four new models were developed through a combination of bond orbital model, Tomlinson's model and Sang's equation. Using Jump energy models, ΔE which is the energy that prevents the tips jump was calculated for Silicon (Si), Zinc Sulphide (ZnS) and Cadmium Sulphide (CdS). Through a combination of Tomlinson model and Sang's equation, temperature model was developed. This model was modified to obtain normal load model. This final model was used to investigate the effects of normal load on nanotribology of silicon. The results obtained compare favourably with experimental results for Si found in literature. Hence the model was used for zinc sulphide and cadinium sulphide. The results show that friction at nanolevel increases with increase in normal load. There are no experimental results for zinc sulphide and cadmium sulphide. Hence, we are predicting experimental results for these semiconductors for the first time using our models.

INDEXING TERMS/KEY WORDS: Nanotribology, Normal load, models, Energy
Academic Discipline: Physics
Method/Approach: Theoritical
Paper type: original research paper

Introduction

Nanotribiology is the study of friction, lubrication and wear at atomistic length and time scales. [1] Extracting information about nanotribological properties of materials is quite a challenging task and requires much interdisciplinary co-operation. Information about nanotribological properties of materials has numerous practical applications. Reducing energetic losses due to friction which will help a car engine to work efficiently, utilizing friction as an operating mechanism eg in

car brakes, reducing material losses due to wear and optimizing lubricants are some important issues for a wide range of industrial and societal applications. [1,2] with the invention of small devices triggered in part by the tremendous development of silicon micro fabrication techniques, novel problems appear that require knowledge at nanometer scale. For example the whole technology of information storage as shown by the case of computer hard desk with dimension that are measured in nanometers. The invention of Atomic Force Microscope (AFM) and Friction Force Microscope (FFM) made the investigation of nanotribological properties of new classes of important materials like insulators and large band-gap semiconductors possible. [3, 4]

Nanotribological properties of Si (100), Z – 15 and Z – 00L (BW) films on Si (100) were investigated. The friction force versus normal load curves were measured by making friction force measurements at increasing normal loads. The results obtained for Si (100), Z – 15 and Z – Dol (BW) films on Si (100) show approximately linear response for all the three samples in the load range of 5 – 130nN. [5] Sundararajan and Bhushan (2001) studied the static friction force on silicon micromotors lubricated with Z – DoL by AFM. Their results show that friction increases with the increase in normal load. [6]

(Liang *et al*, 2003) studied the load dependence on nanotribology of C_{60} using atomic force microscope at different temperatures. Their results show that naanotribology increases with increase in normal load. [7]

Presently, effective laboratory equipment for nanotribological research like AFM and FFM are almost non existent in Africa. Hence, we decided to develop workable theoretical models which can be used to predict experimental results on load dependence of nanotribology over a wide range of semiconductors including semiconducting binary compounds.

The models were used to study the effects of normal load on nanotribiology of Silicon. The results obtained compare favourably with experimental results found in literature. Hence the models were also used for Zinc Sulphide and Cadmium Sulphide

MATERIALS AND METHODS

Four different models were developed and used for this work. The first two were developed through a combination of bound-orbital model and Tomlinson model.

DEVELOPMENT OF JUMP ENERGY MODELS FOR HIGH AND LOW IONIC ENERGY GAPS

From Tomlinson model, the equation describing the thermal effects on atomic friction is given by

$$\frac{dp(t)}{dt} = -F_0 \exp\left(\frac{-\Delta E(t)}{K_B T}\right) P(t) \quad (1)$$

Where F_0 is the characteristic frequency of the system. If we replace time with the lateral force F_L we have

$$\frac{dp(F_L)}{dF_L} = -F_0 \exp\left(\frac{-\Delta E(F_L)}{K_B T}\right) p(F_L) \quad (2)$$

From this model, the force preventing the tips jump is ΔE which is the energy barrier.

$$\Delta E = E(X_{max}, t) - E(X_{min}, t) \quad (3)$$

Where X_{max}. corresponds to the first maximum observed in the energy profile and X_{min} is the actual position of the tip. The quantity ΔE decreases with the frictional force F_L until it vanishes when $F_L = F^*$. Close to the critical point, the energy barrier can be written approximately as

$$\Delta E = \mu (\bar{F} - F_L) \quad (4)$$

Where $\bar{F}$ is close to the critical value F*

In terms of the lattice parameter ‘a’

This energy barrier ΔE is given by

$$\Delta E = \frac{\hbar^2}{2m} \left(\frac{2\pi}{a}\right)^2 \quad (5)$$

Simplifying equation (9) we have

$\Delta E = \frac{h^2}{4\pi^2 2m} \times \frac{4\pi^2}{a^2}$ ----------(6)

$\Delta E = \frac{h^2}{2m}\frac{1}{a^2}$ ----------(7)

In bond-orbital model in binary compounds, if the imaginary (polar) components are present, then the average bond energy gap is

$E_g = -(V_2 + iV_3)$ ---------- (8)

The magnitude of the above energy gap is

$E_g = (V_2^2 + V_3^2)^{½}$ ----------(9)

Using equation (7) $\Delta E = E_T$ was calculated for Si, ZnS and CdS. Comparing the results obtained with that obtained using bond obital model, we found that the calculated values of $\Delta E = E_T$ using Tomlinson model is related to E_g (from bond-orbital model) by the equation

$E_{os} = \beta\,[E_g - (\propto_c^{½} + f_i^2)]$ ----------(10)

for $\propto_c \geq 3.85$eV.

Where $\propto_c$ is the ionic energy gap, f_i is the ionicity of the material and β is an empirical constant and has the value $\beta = 1.073$.

If $\propto_c < 3.85$eV, then another equation holds and is given by

$E_{os} = \beta\,(E_g - f_i^{½})$ ----------(11)

Equations (10) and (11) are jump energy models for high and low ionic energy gaps respectively which we developed. Jump energy model for low ionic energy

gap (equation 11) was used to generate results for silicon while Jump energy model for high ionic energy gap (equation 10) was used for ZnS and CdS. The results obtained are presented in table 1.

DEVELOPMENT OF TEMPERATURE MODEL

The temperature model was developed through derivation of an equation for F_L i.e friction force, using Tomlinson model and Sang's equation. This derived equation was carefully modified in two stages so that it can be applied over a wide range of semiconductors including binary compounds. The first stage of modification produced a good model for investigating temperature dependence of nanotribology and the second stage of modification produced the model used in this work.

From Tomlinson model, the motion of the tip is influenced by

1. the interaction with the atomic lattice of the surface
2. the elastic deformation of the cantilever

If the cantilever moves with a constant velocity 'V' in x-direction, the total energy of the system is $E_{tot}(x,t) = -\frac{E_0}{2}\cos\frac{2\pi x}{a} + \frac{1}{2}K_{eff}(Vt - x)^2$ ----------(12)

At any time't', the position of the tip can be determined by equating to zero the first derivative of the expression $E_{tot}(x,t)$ with respect to x to obtain

$\frac{dE_{tot}}{dx} = \frac{\pi E_0}{a}\,\mathrm{Sin}\,\frac{2\pi x}{a} - K_{eff}(Vt-x) = o$ ----------(13)

The critical position x* corresponding to t = t* is determined by equating to zero the second derivative of the E_{tot} (X, t) to give

$$x^* = \frac{a}{2\pi} \arccos\left(-\frac{1}{y}\right) \text{----------} (14)$$

$$y = \frac{2\,\pi^2 E_o}{k_{eff}\, a^2} \text{----------} (15)$$

when t = t*, the tip suddenly jumps into the next potential profile. The lateral force F* which induces the jump is given by

$$F^* = K_{eff} \frac{a}{2\pi} \sqrt{y^2 - 1} \text{----------} (16)$$

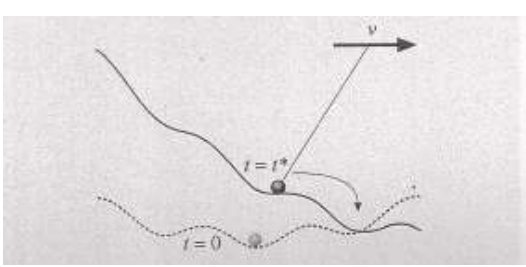
Therefore the stick slip is observed only when y > 1 i.e only when the system is not too stiff.

In two dimensions the energy of the system is

$$E_{tot}(r,t) = U(r) + \frac{K_{eff}}{2}(Vt - r)^2 \text{----------} (17)$$

using the assumption that y >>1, at a given time t = t*, the tip jump is prevented by the energy barrier ΔE. ΔE Decreases with increasing frictions force F_L until is vanishes when $F_L = F^*$.

The figure below shows the energy profile of the system.



Energy profile experienced by FFM tip, (black circle) at t = o (dotted line) and t = t (continuous line)*

Sang observed that the energy barrier ΔE close to the critical point is better approximated by the relation

$$\Delta E = \mu\ (F^* - F_L)^{2/3} \text{ ----------(18)}$$

Where μ = 0.01 as found by mate.

Tomlinson gave the logarithmic dependence of his model as

$$\mu\left(\frac{F^* - FL}{K_B T}\right)^{3/2} = \text{Ln}\ \frac{Vc}{V} - \text{Ln}\ \sqrt{1 - \frac{F^*}{F_L}} \text{ ----------(19)}$$

If V<< V_c, then the [a] second logarithm in equation (19) can be neglected to obtain

$$F_L = F^* - \left(\frac{K_B T}{\mu}\right)^{2/3} \left(\text{Ln}\ \frac{V_C}{V}\right)^{2/3} \text{ ----------(20)}$$

If we take value of V such that $\frac{V_c}{V}$ = e, then the above equation becomes

$$F_L = F^* - \left(\frac{K_B T}{\mu}\right)^{2/3} \text{ ----------(21)}$$

Rearranging equation (18) we have

$$F_L = F^* - \left(\frac{\Delta E}{\mu}\right)^{2/3} \text{ ----------(22)}$$

Adding (21) and (22) we obtain

$$F_L = F^* - \tfrac{1}{2}\left[\left(\frac{\Delta E}{\mu}\right)^{2/3} + \left(\frac{K_B T}{\mu}\right)^{2/3}\right] \text{ ---------- (23)}$$

After series of work with equation (23), we carefully modified it based on the fact that temperature effect on nanotribology requires a more sensitive equation which will predict experimental results more accurately. These modifications led to the equation

$$F_L = F^* - \frac{P^2T^2}{2}\left[\left(\frac{\Delta E}{\mu}\right)^{2/3} + \frac{1}{\mu}\left(\frac{K_BT^2}{\mu}\right)^{2/3}\right] \text{----------}(24)$$

It should be noted that in theoretical modeling multipliers help to improve the sensitivity of a models, hence the introduction of the normalization constant 'P'. The variable 'T' was use as part of the multiplier to help normalize the effect of the constant 'P'

Where p which is an empirical constant is given by P = (R + X)

$R = 1.38 \times 10^{-3}$ and $x = (n_i - 1) \times 10^{-3,}$ n_i takes values from 1- 4.

The above equation is a working model which we have already developed for investigating temperature dependence of nanotribology.

In developing a model for normal load dependence of nanotribology, we note that the above model contains ΔE which has a very essential property of every crystal – lattice spacing, 'a'. The normal load model can be obtained by modification of the above equation.

Dropping $\frac{P^2T^2}{2}$ and substituting L for T^2 in the above model,

We have

$$F_L = F^* - \left(\frac{\Delta E}{\mu}\right)^{2/3} + \frac{1}{\mu}\left(\frac{K\beta L}{\mu}\right)^{2/3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(25)$$

Modifying further and introducing the necessary constants we have

$$F_L = \frac{F^*}{2} + \left[\left(\frac{\Delta E}{\mu}\right)^{2/3} + \left(\frac{K\beta\ L}{\mu^3}\right)^{2/3}\frac{1}{M}\right] + N \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (26)$$

Where M and N are consonants

$M = 1.0 \times 10^{-7}$

$N = (n_i - 1) \times 10^{-9}$ N and

$n_i = 1,2,3, \ldots\ldots$

Hence equation (26) is the normal load model which we developed. The model was used to study the effects of normal load on nanotribology of silicon. The results obtained are in good agreement with experimental results for Si found in literature. Hence, the model was also used for Zinc sulphide and cadmium sulphide. The results obtained for Si together with experimental results found in literature are presented in figure 1 while the results obtained for ZnS and CdS are presented in figure 2.

F* was calculated for each element using equation (16). After series of calculations with different values of y, we adopted y = 100 so as to satisfy the assumption that y>>1.

Results and Discussion

The models were successfully applied to the semiconductors: Silicon, Zinc Sulphide and Cadimium Sulphide. The results obtained using jump energy model for high and low ionic energy gaps are presented in table 1.

Table 1: Results obtained using jump energy model for high and low ionic energy gap.

Material	Lattice spacing (A^o)	Average bond energy gap (eV)	Calculated values of $\Delta E = E_T$ using Tomlinson model (eV)	Calculated values of $\Delta E = E_{os}$ using jump energy models (eV)
Si	5.42	4.77	5.12	5.12
ZnS	5.41	7.85	5.14	5.33
CdS	5.83	7.11	4.43	4.52

The results above show that the values obtained using Jump energy models compare favourably with that obtained using Tomlinson model. Hence with Jump energy models, bond energy gap of every material can be used to calculated ΔE for the material which is the energy that prevents the tip jump. It should be noted that bon-orbital model is an instrument for structural analysis and nanotribology is a structural problem. Hence $\Delta E = E_{os}$ from the table was used in the normal load model for the materials.

The results obtained using normal load model for Si together with the experimental results found in literature are presented in figure 1.below.

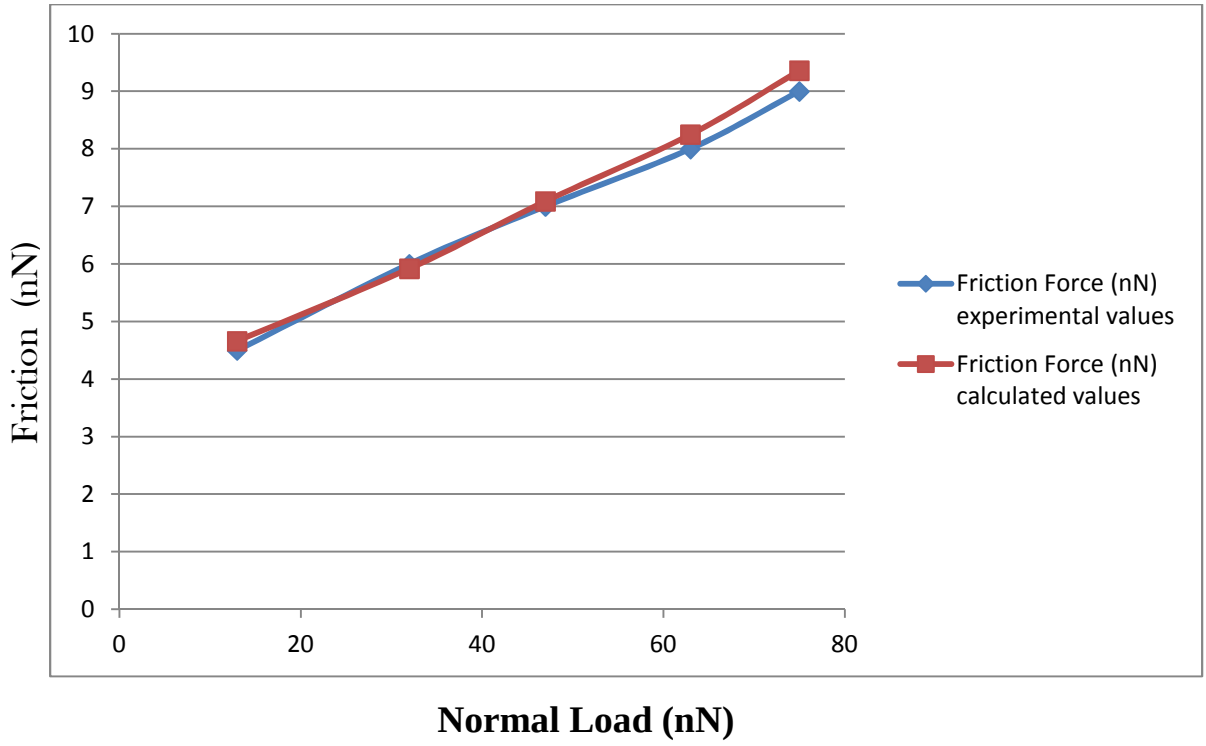


Fig. 1 graphs of the effects of normal load on nanotribology of silicon together with experimental results found in literature.

The graphs above show that the results obtained using the normal load model compare favourably with experimental results for Si found in literature. Hence the model can properly predict experimental results. The model was also used for ZnS and CdS and the results obtained are presented in fig, 2

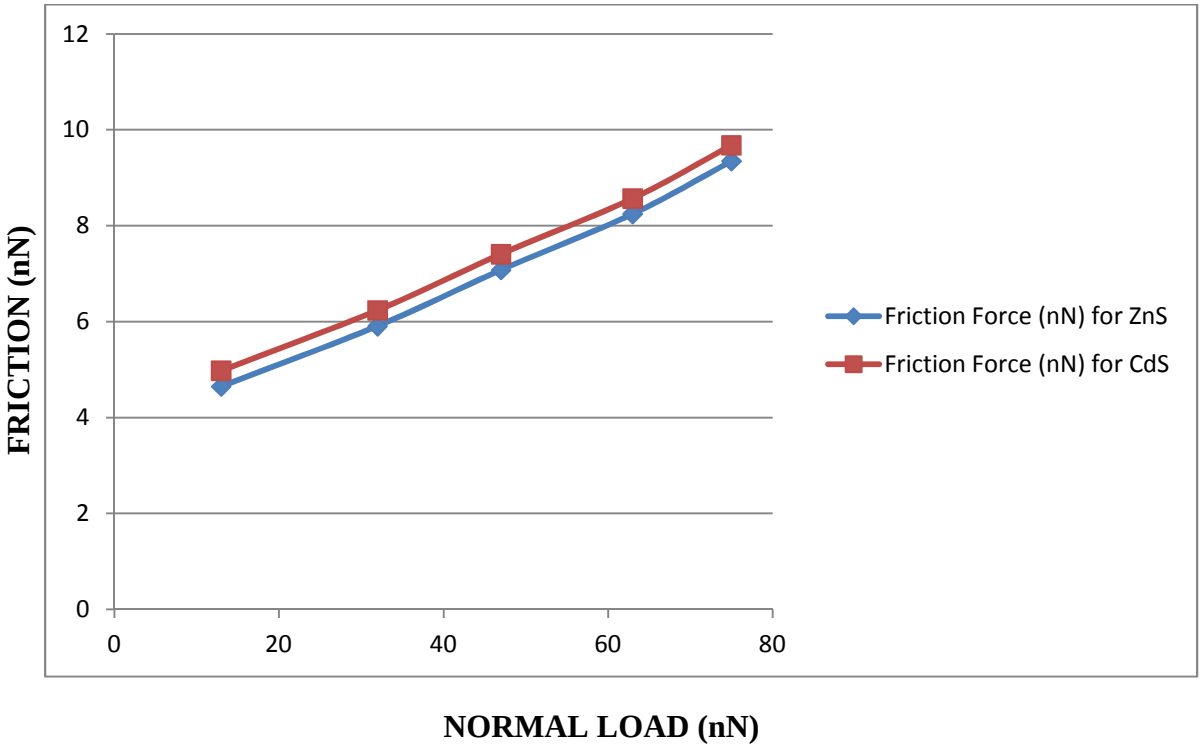


Fig 2: Graphs of the effects of Normal load on Nanotribology of ZnS and CdS.

The above results show that at nano level, friction increases with increase in normal load. This agrees with the experimental results obtained by Carpick (1997), Liang *et al* (2003) and Bennawitz (2004) in which their results show that nanotribology increases with increase in normal load. [9]

The results also indicate that ZnS exhibits better tribological properties than CdS. At a maximum load of 75nN, the nano-friction existing in ZnS is 9.35nN while that of CdS at the same maximum load is 9.68nN.

It therefore follows that zinc sulphide will be a better material in areas where normal load is likely to be high.

Conclusion

The models developed have been applied successfully in the study of the effects of normal load on nanotribology of Si, znS and CdS. The results obtained for silicon actually compare favourably with experimental results found in literature. There are no experimental results for ZnS and CdS. Hence, we are predicting experimental results for these semiconductors for the first time using our models. Nano-friction still stands out as a big challenge in operating systems. Although many breakthroughs have been reported in nanotribology research, much still remains unknown in this area. With more improved research in nanotribology, energetic losses in systems which is the major problem of nano-friction could be

brought under control. The models developed in this work will help immensely towards a more improved research in nanotribology. Presently effective laboratory equipment used in carrying out nanotribology research are Atomic Force Microscope (AFM) and Friction Force Microscope (FFM). These equipment are very difficult to come by in third world countries. Hence the models developed in this work will help scientists in these countries to carry out good research work in nanotechnology.

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