ORIGINAL PAPER

EFFECTS OF TEMPERATURE ON THE NANOTRIBOLOGY OF ZnS AND CdS

SUNDAY I. OLISAKWE [1], AZUBIKE J. EKPUNOBI [2], PETER I. EKWO[2]

Manuscript received: 12.12.2011; Accepted paper: 03.02.2012;

Published online: 10.03.2012

Abstract. *In this work, two models were developed through a combination of bond-orbital model, Tomlinson's model and Sana's equation. Using the first model, ΔE which is the energy burrier that prevents tip jump was calculated for zinc sulphide (ZnS) and cadmium sulphide (CdS). The second model was used to study the effects of temperature on the nanotribology of the two semiconductors. The results obtained using the first model compares favourably with the values of ΔE obtained using Tomlinson's model. The results obtained using the second model compares favorably with experimental results for silicon (Si) found in literature. Hence the model was used for ZnS and CdS. There are no experimental results for ZnS and CdS. Hence we are predicting experimental results for these compounds for the first time using our models.*

Keywords: *nanotribology, temperature, model.*

1. INTRODUCTION

Tribology, the science of friction, wear and lubrication has impact on many fields of science and technology [1]. Consequently, it has been the subject of intense research during the last centuries. Often friction is interpreted as the force needed to plastically deform interlocking asperities of surfaces in relative motion, but more detailed analysis tend to become rather complicated . It has been observed experimentally that friction also occurs in sliding processes without any plastic deformation of the surfaces. This wearless friction is due to instabilities occurring for plastic deformations of the surfaces or from a more atomistic point of view, to the process of "plucking of atoms" proposed by Tomlinson. [2-7]. Roland Bennewitz, (2004) used Tomlinson's model to study temperature dependence of friction on n-hexadecane and octamethycyclotetrasiloxane at nano-level and in each case his results show inverse relationship. Robert A.D. (2002) worked on viscosity of silica. His experimental results show an inverse relationship between temperature and viscosity. Bharat Bhushan (2004) studied the effect of temperature on friction in silicon using a thermal stage attached to Atomic Force Microscope (AFM) and his results show an inverse relationship between the nanotribology and temperature. Due to the level of difficulties encountered by Africans in carrying out research in nanotribology due to lack of necessary equipment like Atomic Force Microscope (AFM), Friction Force Microscope (FFM), we decided to develop workable theoretical models which can be used to predict experimental results. Because experimental

[1]Federal College of Education (Technical), Department of Physics, Umunze, Anambra State, Nigeria.
E-mail: olisaisaac09@yahoo.com.
[2] Nnamdi Azikiwe University Awka, Department of Physics & Industrial Physics, Awka Anambra State, Nigeria.

results for Si are available, these models were used to study the effects of temperature on nanotribology of silicon. The results obtained are in good agreement with experimental results found in literature. Hence the models were used for zinc sulphide (ZnS) and cadmium sulphide (CdS).

Two different models were used for this work. The first one was developed through a combination of bond-orbital model and Tomlinson's model. From Tomlinson's model, the equation describing the thermal effects on atomic friction is given by

$$\frac{dp(t)}{dt} = -f_0 \exp\left(-\frac{\Delta E(t)}{K_B T}\right) p(t) \tag{1}$$

where f_0 is the characteristic frequency of the system. If we replace time with the lateral force f_l we have

$$\frac{dp(f_l)}{df_l} = -f_0 \exp\left(-\frac{\Delta E(f_l)}{K_B T}\right)\left[\frac{df_l}{dt}\right]^{-1} P(f_l)... \tag{2}$$

From this model, the force preventing the tip's jump is ΔE which is the energy barrier.

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

This energy barrier ΔE is given by

$$\Delta E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2 \tag{4}$$

Simplifying equation (4) we have

$$\Delta E = \frac{h^2}{4\pi^2 2m} \cdot \frac{4\pi^2}{a^2}$$

$$\Delta E = \frac{h^2}{2m} \cdot \frac{1}{a^2} \tag{5}$$

In bond-orbital model in binary compounds, if the imaginary (Polar) component and real (covalent) component are present, then the energy gap.

$$E_g = -\left(V_2^2 + iV_3^2\right) \tag{6}$$

But if the imaginary (polar) part varnishes, then the overlap integral contains only the covalent (real) part [8] so that $E_g = \left(V_2^2 + V_3^2\right)^{\frac{1}{2}}$ (7)

Using equation (5), $\Delta E = E_T$ was calculated for Si, ZnS and CdS. Analysis of the results obtained shows that the calculated values $\Delta E = E_T$ using Tomlinson's model is related to E_g (from bond-orbital model) by the equation.

$$E_{TS} = \beta\left(E_g - \left(\alpha_c^{\frac{1}{2}} + f_i^2\right)\right) \tag{8}$$

for $\alpha_c \geq 3.85\ eV$

Where α_c is the ionic energy gap, f_i is the iconicity of the material and β is an empirical constant and has the value β = 1.073. If $\alpha_c < 3.85\ eV$, then equation (8) is modified to:

$$E_{TS} = \beta\left(E_g - f_i^{\frac{1}{2}}\right)... \tag{9}$$

Equation (9) was used for silicon while equation (8) was used for ZnS and CdS. The results obtained are presented in table 1.

The second model was developed through derivation of an equation for F_l i.e friction force using Tomlinson's model and Sang's equation. This derived equation was carefully

modified so that it can be applied over a wide range of semiconductors including binary compounds.

From Tomlinson's model, the motion of the tip is influenced by:

i. The interaction between the atomic lattices of the surface;
ii. 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

$$E_{tot}(x,t) = -\frac{E_0}{2}\cos\frac{2\pi x}{a} + \frac{1}{2}K_{eff}(Vt - x)^2 \tag{10}$$

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

$$\frac{dE_{tot}}{dx} = \frac{\pi E_0}{a}\sin\frac{2\pi x}{a} - K_{eff}(Vt - x) = 0 \tag{11}$$

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

$$X^* = \frac{a}{4}\arccos\left(-\frac{1}{y}\right) \tag{12}$$

$$y = \frac{2\pi^2 E_0}{K_{eff}a^2} \tag{13}$$

When $t = t^*$, the tip suddenly jumps into the next minimum of the potential profile. The lateral force $F^* = K_{eff}(Vt - x^*)$ which induces the jump can be calculated from (11) and (13) to give

$$F^* = K_{eff}\frac{a}{2\pi}\sqrt{y^2 - 1} \tag{14}$$

Therefore the stick-slip is observed only when Y>1 i.e only when the system is not too stiff. The Fig.1 shows the energy profile of the system.

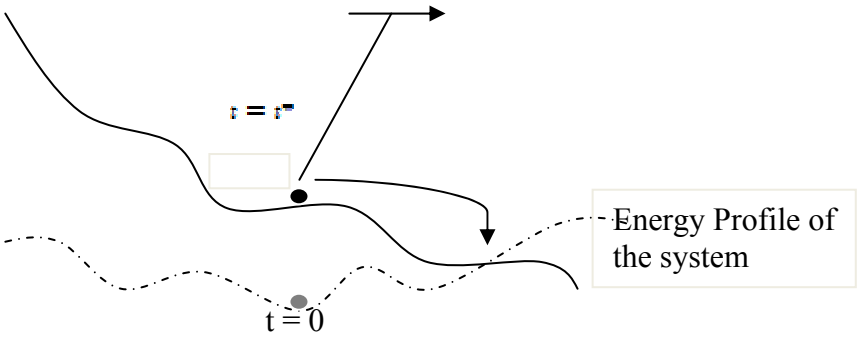

Fig. 1. Energy profile experienced by the FFM tip (black circle) at t=0 (dotted line) and t=t* (continuous line) [9].

In two dimensions, the energy of the system is:

$$E_{tot}(r,t) = U(r) + \frac{K_{eff}}{2}(vt - r)_2 \tag{15}$$

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 frictional force F_l until it vanishes when

$F_l = F^*$. Sang observed that the energy barrier ΔE close to the critical point is better approximated by:

$$\Delta E = \mu(\llbracket F^* - F_l) \rrbracket^{\frac{3}{2}} \tag{16}$$

Where μ=0.01 as found by Mate. Solving equation (16) for F_l, Tomlinson's model gives:

$$\mu \frac{\llbracket (F \rrbracket^* - F_l)^{\frac{3}{2}}}{k_\beta T} = \frac{\ln V_c}{V} - \ln \sqrt{1 - \frac{F^*}{F_l}} \tag{17}$$

Where $V_c = \frac{\pi\sqrt{2}}{2} \frac{F_0 K_\beta T}{K_{eff}}$

If $V << V_c$, then the second logarithm in equation (17) can be neglected to obtain:

$$F_l = F^* - \left(\llbracket \frac{K_\beta T}{\mu} \right) \rrbracket^{\frac{2}{3}} \left(\ln \rrbracket \llbracket \frac{V_c}{\nu} \right)^{\frac{2}{3}} \tag{18}$$

If we take value of V such that $\frac{V_c}{V}$ = e, then the velocity effect on F_1 is suppressed and equation (18) becomes:

$$F_l = F^* - \left(\frac{K_\beta T}{\mu} \right)^{\frac{2}{3}} \tag{19}$$

Rearranging (16) we have:

$$F_l = F^* - \left(\frac{\Delta E}{\mu} \right)^{\frac{2}{3}} \tag{20}$$

Solving (19) and (20) simultaneously we obtain:

$$F_l = F^* - \frac{1}{2} \left[\left(\frac{\Delta E}{\mu} \right) + \left(\frac{K_\beta T}{\mu} \right)^{\frac{2}{3}} \right] \tag{21}$$

After series of work with equation (21), 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 give:

$$F_l = F^* - \frac{P^2 T^2}{2} \left[\left(\frac{\Delta E}{\mu} \right)^{\frac{2}{3}} + \frac{1}{\mu \left(\frac{K_\beta T^2}{\mu} \right)^{\frac{2}{3}}} \right] \tag{22}$$

Where P which is an empirical constant is given by:

$P = (R + x)$, $R = 1.3 \times 10^{-3}$ *and* $x = (n_i - 1) \times 10^{-3}$, n_i takes values from 1 to 4.

Hence equation (22) is the second model which we developed. This equation was used to study the effects of temperature on nanotribology of Zinc Sulphide (ZnS) and Calcium Sulphide (CdS). The results obtained are presented in tables 3 and 4 respectively.

Experimental results for silicon as found in literature together with the results obtained using our model are presented in Table 2.

F^* for each material was calculated using equation (14). After series of calculations with different values of y, we adopted $y=100$ to satisfy the assumption that $y>>1$.

2. RESULTS AND DISCUSSION

The two models were successfully applied to two semiconductors Zinc sulphide and calcium sulphide. The results obtained using first model; equations (8) and (9) are presented in Table 1.

Table 1. The results obtained using first model equations (8) and (9).

Material	Lattice spacing a [A^o]	Average bond energy gap E_g [eV]	Calculated values of $\Delta E=E_T$ using Tomlinson's model [eV]	Calculated values of $\Delta E=E_{TS}$ using equations (8) and (9) [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

These results show that the values obtained using equations (8) and (9) compare favorable with that obtained using Tomlinson's model. Hence with equations (8) and (9), bound energy gap of every material which is obtained from bound – orbital model can be used to calculate ΔE for the material which is the energy that prevents the tip jump. The above results show that ZnS has a higher value of ΔE than CdS. Since ΔE decreases with increasing friction force, it follows that ZnS exhibits better tribological properties at nano level than CdS. It should be noted that bound – orbital model is an instrument for structural analysis and nanotribology is a structural problem. Hence $\Delta E = E_{Ts}$ from the table was used in the second model equation (22) for the two materials and Silicon. The results obtained using the second model for Si together with the experimental results from literature is presented in Table 2.

Table 2. Results obtained for Si using equation (22) (second model), and experimental results.

Temperature [K]	Friction Force Experimental Results [nN]	Friction Force Calculated Values [nN]
298	8.50	8.42
323	8.50	7.81
348	6.50	6.51
373	3.5	4.17
398	3.00	3.07

Experimental results from [10].

The table above shows that the results obtained using equation (22) (second model) for silicon compares favorably with experimental results. The higher deviation observed in the two tables at 373K could be attributed to the fact that in the graph of the experimental data the point plotted for friction at 373K is the only point that falls well off the line of best fit. This is observed in the graph of the results as found in literature. Hence the model can properly predict experimental results. This model was also used for ZnS and CdS and the results obtained are prevented in Tables 3 and 4 respectively.

Table 3. Results obtained for ZnS using the second model.

Temperature [K]	Friction Force [nN]
298	8.40
323	7.80
348	6.51
373	4.15
398	3.05

Table 4. Results obtained for CdS using the second model.

Temperature [K]	Friction Force [nN]
298	9.07
323	8.46
348	7.16
373	4.82
398	3.75

The above results show that friction at nano level decreases with increase in temperature. This agrees with the results obtained by Robert H.D (2002), Bhushan, B. (2004) and Bennewitz, R. (2004) The results also indicates that ZnS has a better tribological properties than CdS at various temperatures. Cadmium sulphide exhibits high value of friction at low temperature. However as the temperature increases, the friction went down to a low value.

3. CONCLUSIONS

The two model developed have been applied successfully in the study of the effects of temperature on the nanotribology of ZnS and CdS. There are no experimental results for ZnS and CdS.

Hence, we are predicting experimental results for these semiconductors for the first time using our model. Bringing friction to a halt remains a big challenge to scientists and technologists.

With the results observed in this work, if micro and nano- electromechanical systems are designed to operate normally at fairly high temperatures, their efficiency will surely increase due to decrease in nanotribology.

REFERENCES

[1] Holscher, H., Udo, E.B., Schwarz, D., *Phys. Rev. Lett.*, **101**, 246105, 2008.
[2] Gyalog, T., Thomas, H. Z., *Physics B*, **104**, 669, 1997.
[3] Frenken, J., *Nature nanotechnology, News and Views,* **1**, 20, 2006.
[4] Chandross, M, Webb, E.B., Stevens, M.J., Grest, G.S. *Physical Review letters,* **93**(16), Article Number: 166103, 2004.
[5] Fraxedas, J., Gracia-Manyes, S., Gorostiza, P., Sanz, F., *Proceedings of the National Academy of Sciences of the United States of America (PNAS)*, **99**(8), 5228, 2002.
[6] Carpick, R.W., Salmeron, M., *Chem. Rev.,* **97**, 1103, 1997.
[7] Robert, H.D., *J. Appl. Phys.,* **92**, 7619, 2002.
[8] Animalu, A.O.E., *Intermediate Quantum Theory of Crystalline Solids*, Prentice-Hall Inc, New Jersey, 1997.
[9] Bennewitz, R**.,** *Friction and Wear on the Atomic Scale, Handbook of Nanotechnology*, Ed. Springer –Verlag Berlin Heidelberg, 2004.
[10] Bhushan B.**,** *Nanoscale Boundary Lubrication Studies, Handbook of Nanotechnology*, Ed. Springer –Verlag Berlin Heidelberg, 2004.