Chalcogenide Letters Vol. 9, No. 7, July 2012, p. 307 - 313

EFFECTS OF TEMPERATURE ON THE NANOTRIBOLOGY OF ZINC SELENIDE (ZnSe) AND CADMIUM SELENIDE (CdSe)

SUNDAY I. OLISAKWE*, AZUBIKE J. EKPUNOBI[a], PETER I. EKWO[a]
Department Of Physics Education Federal College Of Education (Technical), Umunze. Anambra State, Nigeria
[a]*Department Of Physics & Industrial Physics, Nnamdi Azikiwe University Awka, Nigeria.*

Research work in nanotribology is fast growing with promising results. We developed two models for nanotribology research. The first model was developed through a combination of bond- orbital model and Tomlinson's model. Using this model, ΔE which is the energy barrier that presents the tip's jump was calculated for, Zinc Selenide and Cadmium Selenide. The results obtained are in good agreement with those obtained using Tomlinson's model. The second model was developed through a combination of Tomlinson's model and Sang's equation. Because experimental results for Silicon are available, this model was used to study the effects of temperature on the nanotribology of silicon. The results obtained are in good agreement with experimental data for Si found in literature. Hence this model was used to study the effects of temperature on nanotribology of ZnSe and CdSe. There are no experimental results for ZnSe and CdSe. Hence we are predicting experimental results for these compounds for the first time using our models.

(Received May 28, 2012; Accepted July 10, 2012)

Keywords: Nanotribology, Temperature, Model.

1. Introduction

Nanotribology is the study of the atomic scale ingredients of interactions between surfaces in relative motion, such as friction, adhesion, lubrication and wear [1]. These tribological properties have been widely investigated. Many researches on the tribology of various materials have been reported using macroscopic instruments such as surface force apparatus (SFA)[2], or atomic force and friction force microscopy (AFM and FFM) which are particularly designed for measuring the force between a probe tip and a surface both statically and dynamically as well as the topographic pattern of surfaces [2-4].

The increase in the surface -to- volume ratio that occurs when devices are scaled down in size makes friction increasing problematic in miniature instruments, such as micro- and nanoelectromechanical systems. Systems with moving components that come into contact with each other suffer enormous problems due to stiction, friction and wear. More delicate but perhaps less practical ways to reach ultra low friction involve either an extreme reduction of the contact pressure or a cancellation of lateral forces. [5,6,7] The main goal of this work is to develop theoretical models which can be used to study the variation of lateral forces at different temperatures in nano-electromechanical systems (N E M S) and to ensure that these models can predict experimental results.

Roland Bennewicz, (2004) used Tomlinson's model to study the Temperature dependence of friction on n- hexadecane and octame-thylcyclotetrasiloxane at nano-level and in each case his results show inverse relationship. [7]

*Corresponding author : olisaisaac09@yahoo.com

Robert H.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 nanotribiology of silicon using a thermal stage attached to Atomic force microscope (A F M) and his results show an inverse relationship between temperature and friction force. In this work, we developed theoretical models which can be used to predict experimental results. These models were used to study the effects of temperature on nanotribiology of silicon. The results obtained are in good agreement with experimental results found in literature. Hence the models were also used for Zinc Selenide (ZnSe) and Cadmium Selenide (CdSe).

2. Materials and methods

Two models were developed and 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

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

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 **Δ**E which is the energy barrier.

$$\mathbf{\Delta}\mathrm{E} = (\mathrm{X}_{\mathrm{max},}\ \mathrm{t}) - (\mathrm{X}_{\mathrm{min},}\ \mathrm{t}) \tag{3}$$

This energy barrier ΔE is given by

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

Simplifying equation (4) we have

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

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

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

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

But if the imaginary (polar) part varnishes, then the overlap integral contains only the covalent (real) part [8] so tha

$$\mathrm{t}\ E_g = (V_2^2 + V_3^2)^{\frac{1}{2}} \tag{7}$$

Using equation (5), $\mathbf{\Delta}E = E_T$ was calculated for silicon, zinc selenide and cadmium selenide. Analysis of the results obtained shows that the calculated values of $\mathbf{\Delta}E = E_T$ using Tomlinson's model is related to E_g (from bond-orbital model) by the equation

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

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 $\beta = 1.073$
If $\alpha_c < 3.85\ eV, then\ equation\ (8)\ is\ modified\ to$

$$E_{Ts} = \beta \left(Eg - F_i^{\frac{1}{2}} \right) \quad (9)$$

Equation (9) was used for silicon while equation (8) was used for zinc selenide and cadmium selenide. 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 lattice 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

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

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

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

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

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

$$y = \frac{2\pi^2 E_0}{K_{eff} a^2} \quad (13)$$

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

$$F = K_{eff} \frac{a}{2\pi} \sqrt{y^2 - 1} \quad (14)$$

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

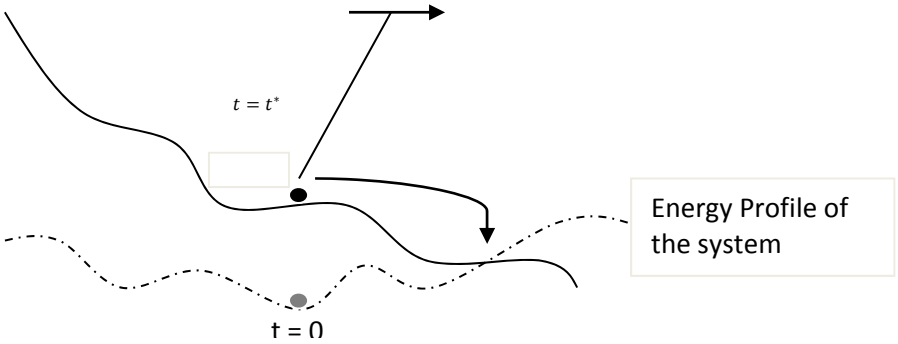

Fig. 1. Energy profile experienced by the FFM tip (black circle) at t=0 (dotted line) and $t=t^*$ (continuous line). Figure taken from [9]

In two dimensions, the energy of the system is

$$E_{t0t}(r,t) = U(r) + \frac{K_{eff}}{2}(Vt - r)^2 \tag{15}$$

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

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

where μ=0.01 as found by Mate.
Solving equation (16) for F_l, Tomlinson model gives

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

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 (17) can be neglected to obtain

$$F_l = F^* - (\frac{K_\beta T}{u})^{\frac{2}{3}} (\ln\frac{V_c}{v})^{\frac{2}{3}} \tag{18}$$

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

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

Rearranging (16) we have

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

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

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

After series of calculations with equation (21), we carefully modified it based on the fact that temperature effects on nanotribology requires a more sensitive equation which can predict experimental results more accurately. These modifications produced the equation

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

Where P which is an empirical constant is given by

$$P = (R + x)$$

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

Hence equation (22) is the second model we developed. Because experimental results for silicon are available, this model was first used to study the effects of temperature on the nanotribology of silicon and then ZnSe and CdSe. The results obtained for silicon together with the experimental results found in literature are presented in table 2. The results obtained for ZnSe and CdSe using the same model are presented in tables 3 and 4 respectively.

F^* for each material was calculated using equation (4). After series of calculations with different values of y, we adopted y=100 to satisfy the assumption that y >> 1.

3. Results and discusion

The two models were successfully applied to the two semiconductors under study ZnSe and CdSe. The results obtained using the first model are presented in table 1 below.

Table 1.

Material	Lattice spacing a(A^0)	Average bond energy gap E_g(ev)	Calculated values of ΔE= E_T using Tomlinson's model (eV)	Calculated values of **Δ**E=E_{Ts} using equations (8) and (9) (eV)
Si	5.42	4.77	5.12	5.12
Znse	5.67	7.05	4.68	4.60
Cdse	6.05	6.58	4.12	4.02

Results obtained using the first model, Equations (8) and (9)

These results show that the values obtained using equations (8) and (9) compare favorably with those obtained using Tomlinson's model. Hence with equations (8) and (9), bond energy gap of every material which is obtained from bond- orbital model can be used to calculate ΔE, which is the energy that prevents the tip's jump. The above results show that ZnSe has higher value of ΔE than CdSe.

Since ΔE decreases with increasing friction force, it follows that ZnSe exhibits better tribological properties at nano level, than CdSe. It should be noted that the bond-orbital model is an instrument for structural analysis and nanotribology is a structural problem. Hence ΔE=E_{Ts} from the table was used in the second model for the three materials. The results obtained using the

second model for Si together with the experimental results found in literature are presented in table 2.

Table 2

Temperature (K)	Friction Force Experimental Results (nN)	Friction Force Calculated Values (nN)
298	8.50	8.42
323	8.00	7.81
348	6.50	6.51
373	3.50	4.17
398	3.00	3.07

Results obtained using equation (22) (second model) and experimental results for Si Experimental results from [10]

The table above shows that the results obtained using the second model are in good agreement with experimental results. The higher deviation observed in the table 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 used for ZnSe and Cdse. The results obtained are presented in tables 3 and 4, respectively.

Table 3

Temperature (K)	Friction force (nN)
298	8.81
323	8.20
348	6.92
373	4.56
398	3.49

Results obtained for ZnSe using the second model.

Table 4

Temperature (K)	Friction force (nN)
298	9.42
323	8.81
348	7.53
373	5.17
398	4.10

Results obtained for CdSe using the second model

The above results show that friction decreases with increase in temperature. This agrees with the results obtained by Robert H.D, (2002), Bhustan B., (2004) and Bennewitz R., (2004).

The results also show that ZnSe has better tribological properties than CdSe.

4. Conclusion

The two models developed have been used successfully in the study of the effects of temperature on the nanotribology of ZnSe and CdSe. 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 challenging problem to scientists. Frenken J., in his work suggested making use of the non-periodicity of quasicrystals or by introducing a deliberate lattice mismatch between the two sliding crystal surfaces. If micro and nano-electromechanical systems are designed to operate normally at fairly high temperature their efficiency will surely increase due to decrease in nanotribology.

References

[1] R.W. Carpick and /M. Salmeron Chem. Rev. **97,** 1103-1194 **(**1997).
[2] Y. Terada., M. Harada .,T. Ikehara., and T. Mishi., J.Appl.Phys**. 87,** 2803(2000).
[3] J. Frenken, News And Views, Nature Nanotechnology **1**, 20-21(2006).
[4] Q. Liang ., O.K.C. Tsui ., Y. Xu ., H. Li ., and X. Xiao . Physical Review Letters. **90,**146102**,** (2003),
[5] M. Chandross E.B. Webb III., M.J. Stevens ., and G.S. Grest. Physical Review letters **93,** 166103**,** (2004)
[6] J. Fraxedas ., S. Gracia-Manyes ., P. Gorostiza ., AND F. Sanz. PNAS **99**, 852285232, (2002)
[7] H.D Robert . J. Appl. Phys. **92,** 7619, (2002)
[8] A.O.E Animalu., Intermediate Quantum Theory Of Crystalline Solids. Prentice-hall inc, New Jersey, 300-301, (1997).
[9] R. Bennewitz **,** Friction And Wear On The Atomic Scale In B.Bhushan (Ed) Springer Handbook Of Nanotechnology, Springer –Verlag Berlin Heidelberg, 631, (2004) .
[10] B. Bhushan **,** Nanoscale Boundary Lubrication Studies In B.Bhushan (Ed) Springer Handbook Of Nanotechnology, Springer –Verlag Berlin Heidelberg,861 (2004)