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**ENVIRONMENTAL PERFORMANCE LIMITS OF ULTRANANOCRYSTALLINE  
DIAMOND FILMS**

**Matthew A. Hamilton**

Dept. of Mechanical Engineering and Applied  
Mechanics  
University of Pennsylvania

**Andrew R. Konicek**

Dept. of Physics and Astronomy  
University of Pennsylvania

**David S. Grierson**

Dept. of Engineering Physics  
University of Wisconsin-Madison

**A V. Sumant**

Center for Nanoscale Materials  
Argonne National Laboratory

**W. Gregory Sawyer**

Dept. of Mechanical and Aerospace Engineering  
University of Florida

**Robert W. Carpick**

Dept. of Mechanical Engineering and Applied  
Mechanics  
University of Pennsylvania

**ABSTRACT**

Recent improvements in growth methodologies have decreased the grain sizes and thicknesses of polycrystalline diamond films to the nanometer range, while also increasing the film uniformity and growth rate and preserving the outstanding mechanical properties of diamond. This is rendering such films more technologically and commercially viable. Ultrananocrystalline diamond (UNCD) are the thinnest (<200 nm) and smoothest ( $R_q < 10$  nm) diamond films available.[1] These films demonstrated self-mated friction coefficients as low as near frictionless carbon ( $\mu < 0.007$ ) in environments with sufficient humidity, and the corresponding wear rates could not be measured using scanning white-light interferometry. However, their response to environmental conditions (e.g. relative humidity, ambient species, velocity, and temperature) had not been systematically explored in the past. This study focused on identifying conditions that contribute to favorable tribological performance. We find low friction performance at humidity levels below 1.5% in both nitrogen and argon environments.

**INTRODUCTION**

Since their development, diamond films have demonstrated a variety of favorable properties. These films have hardness values close to 100 GPa with modulus values approaching 1000 GPa.[2] The thermal conductivity of diamond films is nearly 5 times that of copper. This combination of properties makes it ideal for coating machine tools where hardness and thermal conductivity dictate cutting performance. However, as a solid

lubricant diamond has shown poor performance in low humidity environments. Also, micro and nanocrystalline diamond films have roughness values comparable to their grain sizes (1-10 $\mu$ m and 100-300nm respectively). Hayward *et al.* showed the roughness of these films dictated friction performance.[3] As a result, diamond like carbon films have been commonly used as solid lubricants because of their extremely low roughness ( $R_q < 1$  nm). More recently improvements in the growth processes for diamond films have reduced the grain sizes in diamond films to below 10 nm. These films are termed ultrananocrystalline diamond (UNCD), and have roughness values comparable to the diamond grain size. Konicek *et al.* reported friction coefficients of 0.03 to 0.01 for these films in a humidified argon environment.[4] This paper reports on the investigation of these films in humidified nitrogen environments. The response of these films to varying humidity and varying exposure time at fixed humidity is reported.

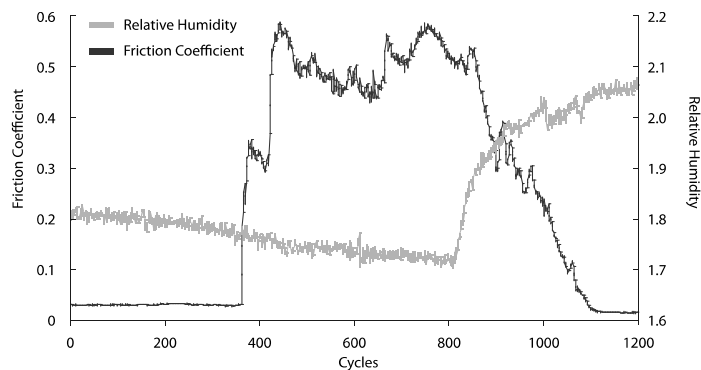
**Experimental**

All friction testing was performed using a linear reciprocating tribometer described in detail by Dickrell *et al.* The sample geometry was pin-on-flat using a 1/8" diameter silicon-nitride sphere and silicon flat. Both the pin and the flat were coated with UNCD creating a self-mated interface. A smaller environment chamber was constructed to reduce the time constant for changing humidity and allow for more precise

control of ambient species throughout the testing. The level of humidity in the environment was controlled by mixing a dry nitrogen gas with nitrogen gas bubbled through water. Both lines were connected to flow controllers so the ratio of dry to humidified gas could be adjusted. The exposure time was controlled by changing the sliding speed with a fixed track length and by changing the track length under a fixed sliding speed.

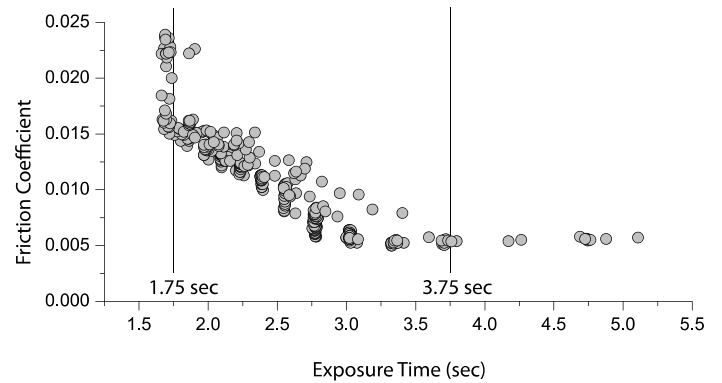
## RESULTS AND DISCUSSION

The first in the series of experiments was performed using a normal load of 1N, a sliding speed of 1 mm/sec and humidity levels were adjusted between 2.0% RH and 1.7% RH producing more than an order of magnitude increase in friction coefficient (from 0.03 to 0.6). This behavior was found to be reversible by increasing the humidity level, but displayed some hysteresis. This response has been seen on multiple occasions and friction was recoverable in all cases.



**Figure 1** Friction coefficient response to changes in relative humidity. The friction spikes like a switch as the humidity drops below 1.75% but does not recover until the humidity increases above 1.90%.

After seeing this behavior, a second set of experiments were performed to test the hypothesis that it was a surface passivation mechanism. In these tests, the humidity was kept in the range of 0.7% but the exposure time was adjusted using sliding speed. Because the friction spike was seen at 1.75% using a sliding speed of 1mm/sec, sliding speeds were adjusted between 200 $\mu$ m/sec to 600 $\mu$ m/sec to ensure long enough exposure time for the humidity in the environment. During this experiment, the sliding speed was ramped in 25 $\mu$ m/sec increments and the friction coefficient response was observed. As exposure time decreased three distinct regions were observed. Above 3.75 seconds the friction remains close to 0.005. From 3.75 to 1.6 seconds there is linear increase from 0.005 to 0.15. Below 1.6 seconds of exposure time, the friction spikes to 0.6. As with the previous experiment, the friction coefficient was recoverable.



**Figure 2** Friction response to varying exposure time. This plot indicates friction is either velocity dependent or surface passivation is occurring and dictating performance.

## CONCLUSIONS

1. There is a limiting relative humidity for self-mated UNCD performance that is below 2.0% for the sliding speed and normal load used in the experiments.
2. Although friction spikes immediately when the threshold is reached, it is recoverable when additional humidity is provided.
3. The steady-state friction coefficient for self-mated UNCD films in nitrogen was on the level of near frictionless carbon (below 0.005).

## ACKNOWLEDGMENTS

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## REFERENCES

1. Lee, Y.C., et al., *Improvement on the growth of ultrananocrystalline diamond by using pre-nucleation technique*. *Diamond and Related Materials*, 2006. **15**(2-3): p. 353-356.
2. Espinosa, H.D. and B. Peng, *A new methodology to investigate fracture toughness of freestanding MEMS and advanced materials in thin film form*. *Journal of Microelectromechanical Systems*, 2005. **14**(1): p. 153-159.
3. Hayward, I.P., I.L. Singer, and L.E. Seitzman, *Effect of Roughness on the Friction of Diamond on Cvd Diamond Coatings*. *Wear*, 1992. **157**(2): p. 215-227.
4. Konicek, A.R., et al., *Origin of ultralow friction and wear in ultrananocrystalline diamond*. *Physical Review Letters*, 2008. **In Press**.