Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Amontonian frictional behaviour of nanostructured surfaces

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A. Experimental

i) Preparation of Zinc Oxide Nanograins

Zinc oxide nano-grains were grown on Si (100) substrates using Pulsed Laser Deposition (PLD). In a vacuum chamber the substrates, cleaned by immersing in acetone in an ultrasonic bath and washing with ethanol, were mounted at D = 50 mm from the front surface of the ZnO target (Testbourne, 99.99% purity). The chamber was then evacuated to a base pressure of $1x10^{-6}$ Torr and subsequently back-filled with a steady (10 sccm) flow of oxygen to maintain pO_2 = 10 mTorr. A 250W tungsten halogen quartz bulb was used to heat the substrate to T_{sub} = 300°C and the grain-layer deposited using an ArF excimer laser (193 nm, Lambda-Physik Compex 201, operating at a repetition rate of 10 Hz) at varying *F* for 10 minutes. The ZnO grain-layer coated substrate was then allowed to cool to room temperature in *p*O2 10 mTorr, before the deposition chamber was brought up to air. The deposited grains were analysed and characterized by AFM. As examples AFM images of ZnO nanograins prepared at room temperature at three different incident fluencies are presented in Fig.S1, clearly showing an increase in surface coverage with increasing fluence.

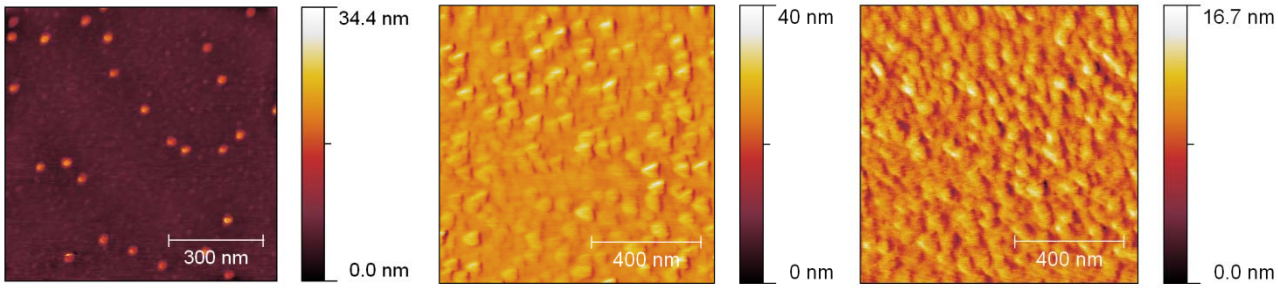

Fig.S1. AFM images of ZnO nanograins prepared at room temperature and an incident laser fluence of a) 7.5 Jcm^{-2}, b) 15 Jcm^{-2} and c) 22.5 Jcm^{-2}.

Table.S1. Measured geometric dimensions and roughness parameters of ZnO nano-grain surfaces.

T_{sub} (°C)	F (J cm^{-2})	RMS (nm)	R_a (nm)	Mean Height (nm)	Maximum Height (nm)	Average grain diameter (nm)
25	7.5	1.64	0.73	4.4	34.40	45
	15	2.27	1.66	14.31	40.00	60
	22.5	1.59	1.23	9.8	16.70	65
300	7.5	1.18	0.93	9.43	17.80	60
	15.0	2.27	1.71	22.46	31.20	80
	22.5	4.48	3.61	17.87	32.30	40

ii) Preparation of Zinc Oxide Nanorods

Zinc oxide nano-rod arrays were grown on Si (100) substrates using a two stage Diffusive PLD (DPLD) method using traditional PLD to grow an initial grain-layer, then reversing the substrate and continuing growth on the grain layer facing away from the abalation target [1]. The grain layers were first grown for 10 minutes at T_{sub} = 300°C and F = 4 J cm^{-2}. The chamber was then allowed to cool to room temperature in pO_2 = 10 mTorr, before the deposition chamber was brought up to air and the substrate reversed. The chamber was then evacuated again to a base pressure of 1x10^{-6} Torr and back-filled with oxygen to maintain pO_2 = 10 mTorr. The substrate was then heated to 600°C and the rods deposited for 10 minutes using F = 4 J cm^{-2}. Again, the ZnO grain-layer coated substrate was allowed to cool to room temperature in pO_2 = 10mTorr, before the deposition chamber was brought up to air. The deposited rods were analysed and characterized by SEM and AFM.

Table.S2. Measured geometric dimensions and roughness parameters of ZnO nano-rod surfaces.

Rod length (nm)	Rod diameter (nm)	RMS (nm)	R_a (nm)	Mean Height (nm)	Maximum Height (nm)
225	20	4.1	3.2	17.5	36.4
450	20	43.4	34.5	133.6	304.5
600	20	51.5	41.6	217.7	393.9
720	20	19.4	15.8	63.6	122.7

iii) Preparation of Nanocrystalline Diamond

Nano-crystalline diamond (NCD) films were grown by MWPECVD in a 2.45 GHz reactor on 1 cm^2 polished Si (100) substrates as described by Fox *et al.* [2] . The substrates were first seeded with 5 nm

detonation diamond powder, applied by electrospraying a diamond, PVP and methanol suspension to form a homogenous seed layer[3], then placed in a Mo holder inside the reactor, on top of a tungsten wire ring that acts as a thermal barrier. The reaction chamber was then evacuated, a flow of the appropriate gas mixture was introduced and the pump throttled to establish the required operating pressure *p* and flow rate (520 sccm). Typical gas mixtures used in depositing each NCD film comprised 1% H_2, 1% CH_4 and 98% X (where X= He, Ne, Ar, Kr, all 99.9% pure) though the optimum deposition parameters (power density, reactor pressure and H_2 fraction) for each inert gas were slightly different depending on the stability of the plasma. During deposition substrate temperature, T_{sub}, was monitored by a 2-colour optical pyrometer. Post-deposition, the samples (and chamber) were left to cool, the latter was then brought back up to air and the NCD coated substrate extracted. However, the total gas flow $\boldsymbol{F}_{total}$ was kept constant at 520 sccm. The deposited films were analysed and characterised by SEM and AFM.

Table.S3. Measured geometric dimensions and roughness parameters of nanodiamond films.

Condition	Average Domain Size (nm) (AFM)	Average Crystallite Size (nm) (SEM)	R_a (nm)	RMS (nm)	Mean Height (nm)	Max. Height (nm)
He	216.3	54.8	38.2	49.1	97.2	206
Ne	220.0	44.0	34.8	45.2	245	358
Ar	118.8	34.8	20.5	25.9	79.7	163
Kr	70.0	72.0	35.7	44.7	75.2	174

v) Preparation of Aluminium Oxide Nanodomes

Nanometer sized domes aluminium oxide were grown from a two-step anodic oxidation of high purity (99.997%) aluminium foils (Alfa Aesar) using the method described by Mattia *et al.* [4]. To remove any native oxide layers, each of the foils was electro-polished in a 1:4 mixture of perchloric acid and ethanol. For the 70 nm dome substrates the foil (10 mm in diameter) was mounted on a copper plate, which served as an anode, and exposed to 0.3 M oxalic acid in a thermally insulated electrochemical cell at a constant temperature of 14 °C for 1 hour under an applied potential of 40 V. The alumina was then removed with 1.8wt% chromic acid and 6wt% phosphoric acid solution at 60 °C for 30 minutes. The foils were then rinsed well with deionised water and reimmersed in the 0.3 M oxalic acid electrolyte solution at the same temperature for a further 10-12 hours at the same voltage. Similar methods were used for the 70 nm dome substrates, but the first step was conducted use of 0.5 M sulphuric acid electrolyte at a temperature of 0-3°C for 20 minutes under 20 V potential, and the second step ran for 5-6 hours at the same potential. To remove the aluminium back the substrates were immersed in a 0.2M $CuCl_2$/ 20%HCl solution. Characterisation and analysis of the domes was conducted by AFM.

Table.S4. Measured geometric dimensions and roughness parameters of Al_2O_3 nano-dome surfaces.

Average Dome Diameter (nm)	RMS (nm)	R_a (nm)	Mean Height (nm)	Maximum Height (nm)
40	2.65	2.11	11.98	17.4
70	4.55	3.57	20.00	40.2

References

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