Lecture 15: Two special modes for AFM: Electrostatic Force Microscopy (EFM) and Magnetic Force Microscopy (MFM)

- basic principles and mechanisms of EFM and MFM;
- two scanning modes;
- typical applications: with EFM for applications in interfacial charge transfer and separation, and MFM for exploring the nanostructural magnetic information's (real case studies as inspired from mother Nature).

EFM also called:
scanning electrostatic potential microscopy (SEPM)
(Force → feedback; potential → measurement)

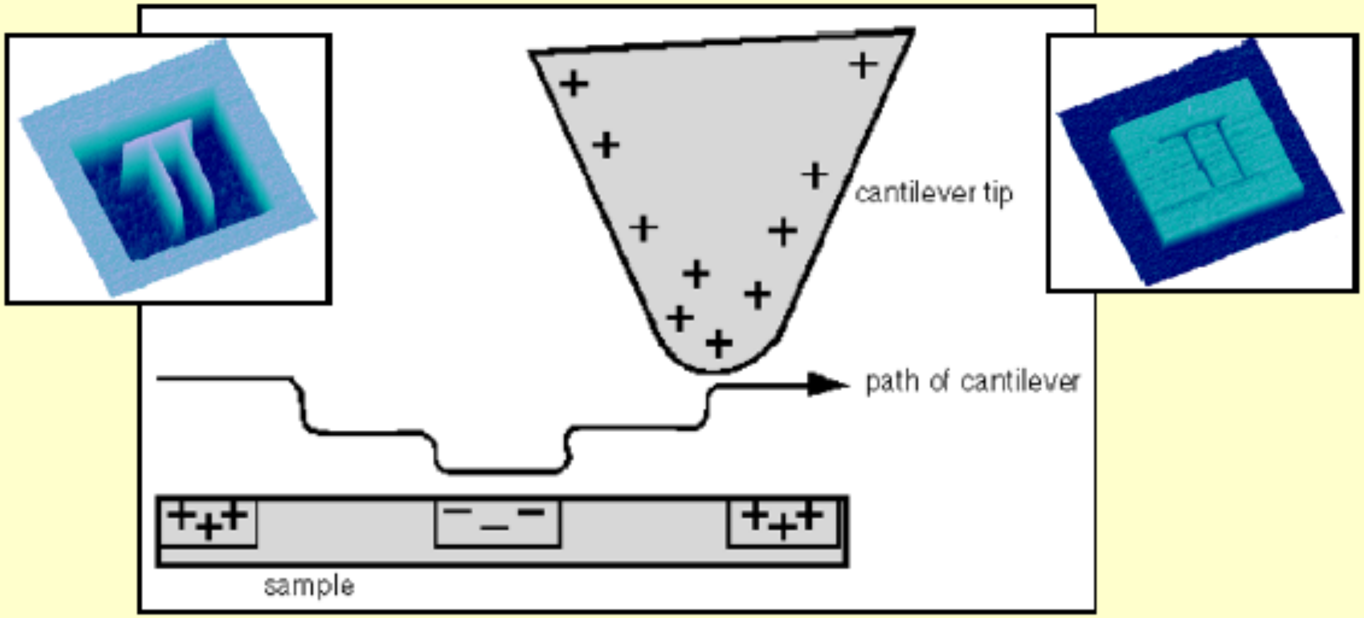
or Kelvin probe force microscopy (KPFM)

What is EFM?

- EFM is a secondary imaging mode derived from AFM.
- EFM measures electric field gradient distribution above the sample surface, through measuring local electrostatic interaction between a conductive tip and a sample .
- In EFM, a voltage is applied between the tip and the sample.
- The bias is used to create and modulate an electrostatic field between the tip and the substrate.
- The cantilever’ s resonance frequency and phase change with the strength of the electric field gradient and are used to construct the EFM image.
- EFM can be used to distinguish conductive and insulating regions in a sample.

What are other secondary imaging modes derived from AFM?

Electrostatic Force Microscopy (EFM)



Electrostatic Interaction Upon Voltage Application

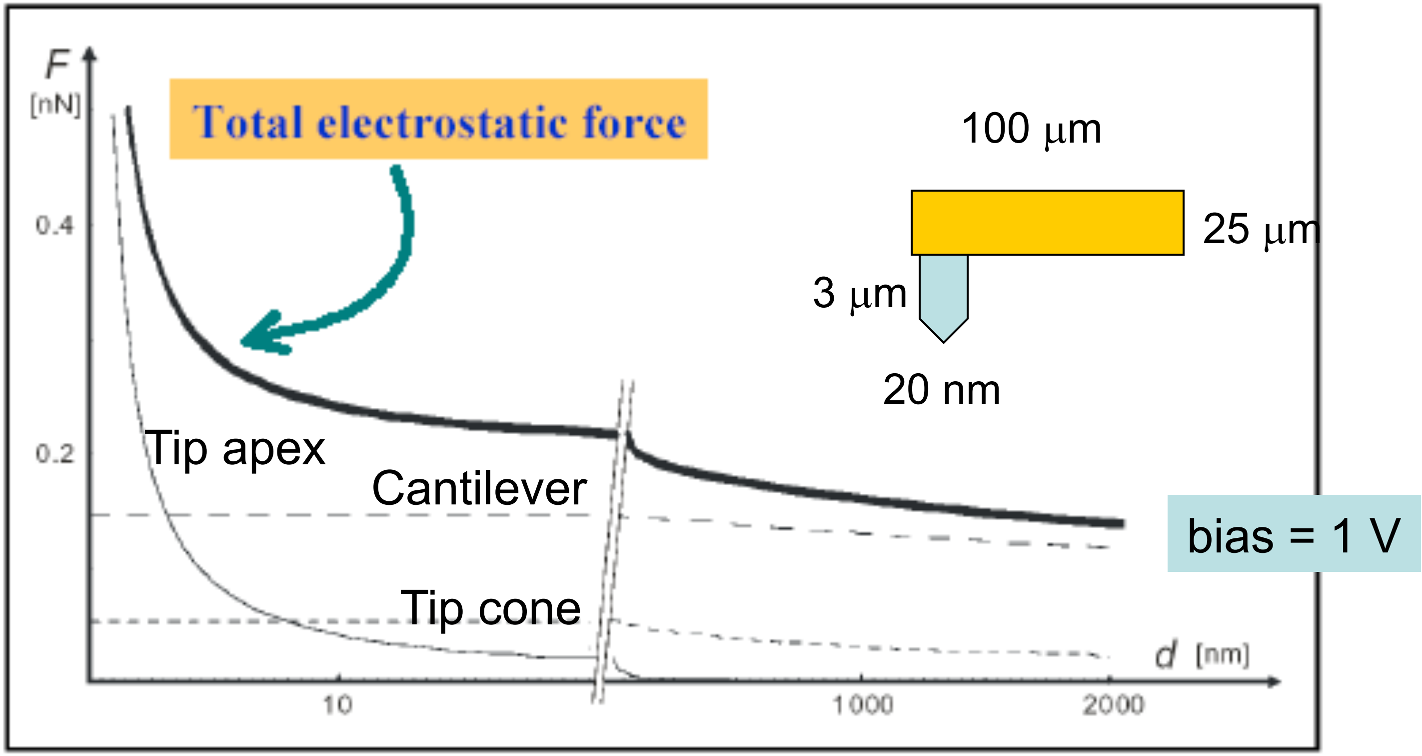
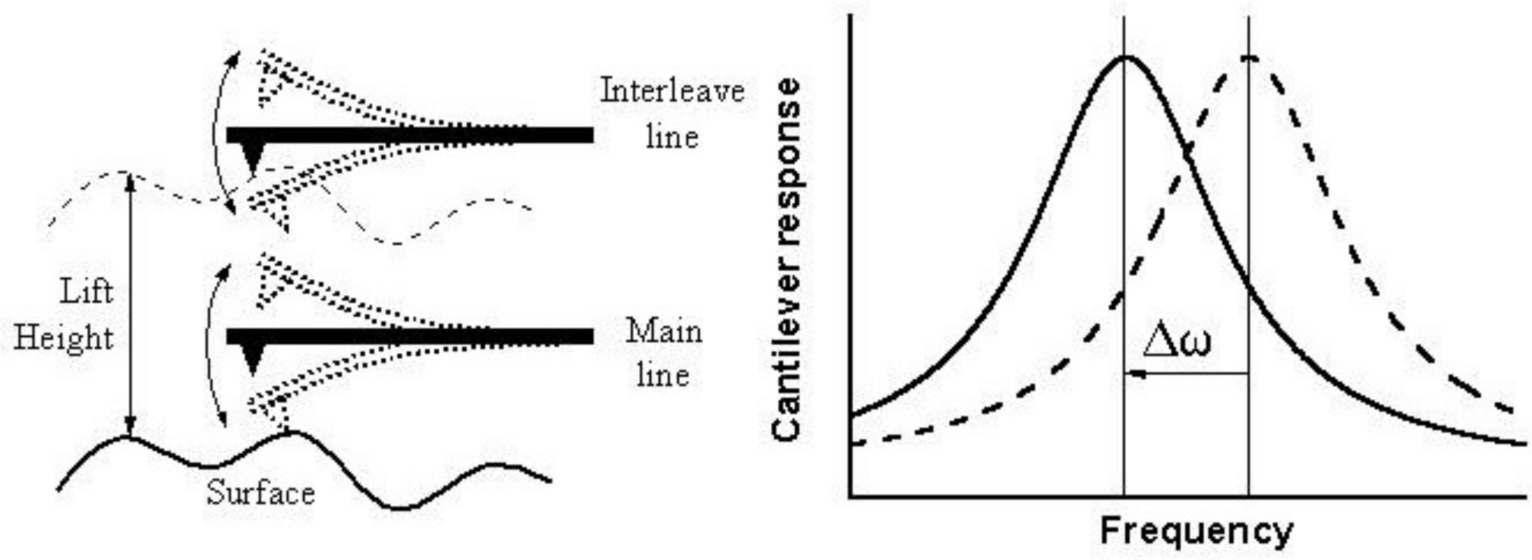
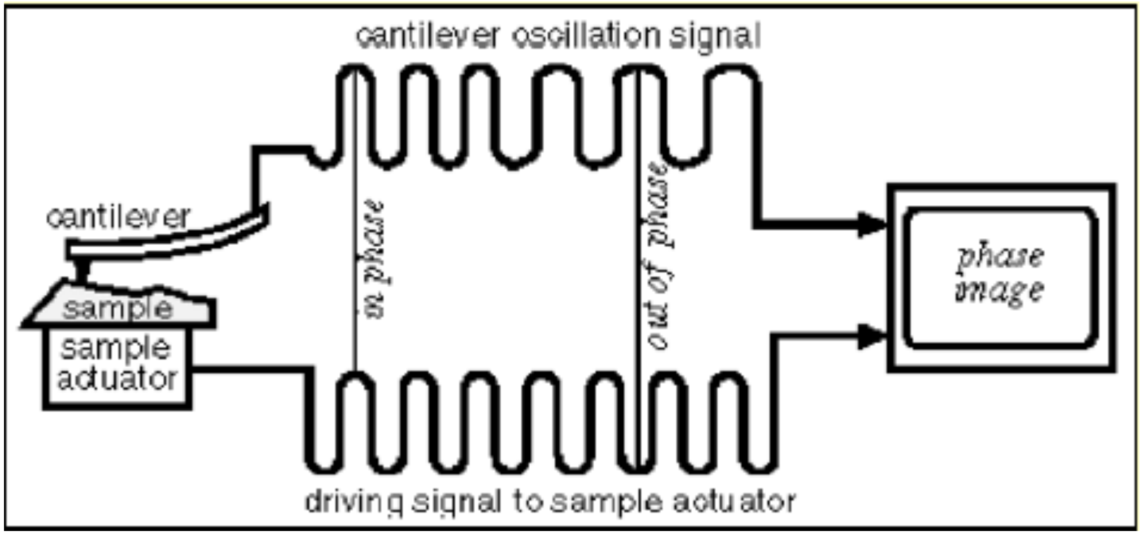


Figure 2.3 Electrostatic force vs. tip-sample distance. The thick solid curve corresponds to the total electrostatic force, while the other three represent separately each of the contributions form the cantilever (dash line), tip cone (short dash) and tip apex (thin solid). These curves have been calculated for U=1 volt, and a probe with dimensions of 100 µm long and 25 µm wide cantilever, 3µm long tip and a radius of 20 nm for the tip apex. The angle for the tip is π/4 and an angle of π/8 was assumed between the cantilever and the sample. These curves were obtained following the model proposed in [Colchero submitted].

Cantilever frequency change due to electrostatic interaction



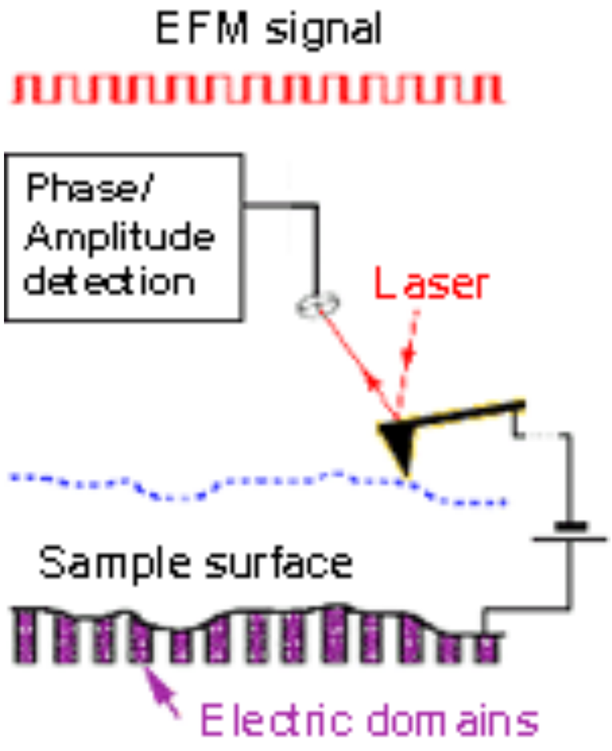
Phase Imaging



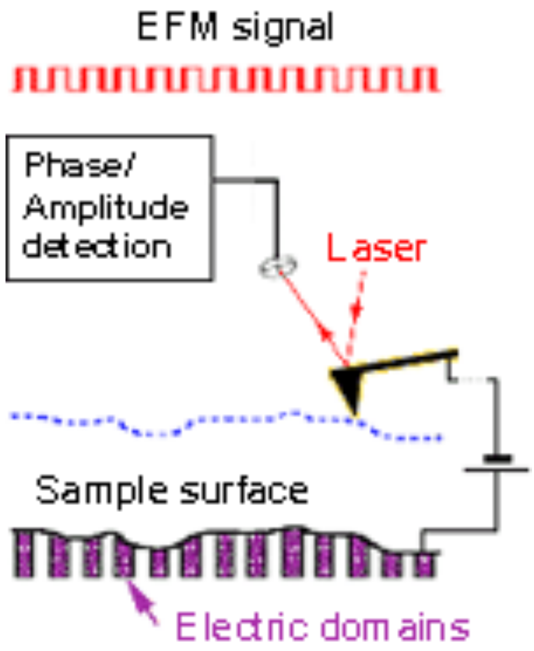
Two types of EFM measurement:

1. Lifted mode: constant height

- Because the electrostatic forces interact at greater distances than van der Waals forces, so electrical force information can be separated from surface topography simply by increseasing the tip-to-sample distance --- lift up the tip.
- Dual scanning --- Grounded tip (no bias) first acquires surface topography in the tapping mode, then the tip is lifted up (typically 5-50 nm), and retraces the surface profile maintaining **constant tip-surface distance**.
- A constant voltage is maintained on the tip. As the tip moves over an attractive electric field gradient, it is pulled toward the sample. When the tip traverses a repulsive gradient, it is pushed away from the sample.
- The deflection (or frequency change) of the cantilever, proportional to the charge density, can be measured using the standard light-lever system.



Lifted mode scanning



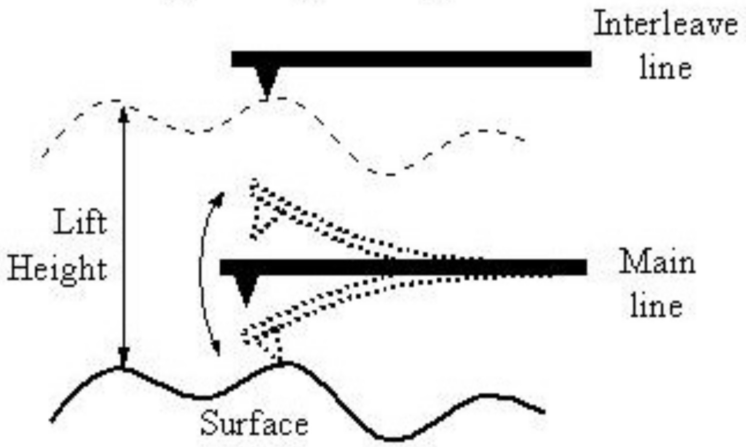
- The electrostatic interaction is also dependent on distance;
- To map the surface charge (potential) distribution, it is crucial to keep the tip scanning at constant height to remove the effect of surface fluctuation (topography) --- *background subtraction*;
- Thus, the measured surface density of charge can be correlated to the 2D distribution on surface or within surface layer.

Two types of EFM measurement:

2. Variable bias: constant deflection

- Measuring the surface potential (charge) on the sample by adjusting the voltage on the tip.
- In order to maintain feedback, the applied voltage on the cantilever is adjusted such that a constant amplitude or deflection is maintained.
- Images can be collected in DC (contact mode) by recording the deflection of the cantilever or by AC mode (tapping mode) where the cantilever is oscillated above the surface and either the phase or amplitude of the cantilever is recorded.

$$V_{tip} = V_{dc} + V_{ac}\cos\omega t$$



Total force between tip and sample

Total force
= capacitive force + Coulomb interaction + van der Waals force + hard-sphere repulsion.

$$F_{\mathrm{EFM}} = \frac{1}{2}\frac{\mathrm{d}C}{\mathrm{d}z}(V_{\mathrm{b}}+\varphi)^2 - E_Z C(V_{\mathrm{b}}+\varphi) + \underbrace{F_{\mathrm{VDW}} + F_{\mathrm{hs}}}_{\text{Atomic force: small}}$$

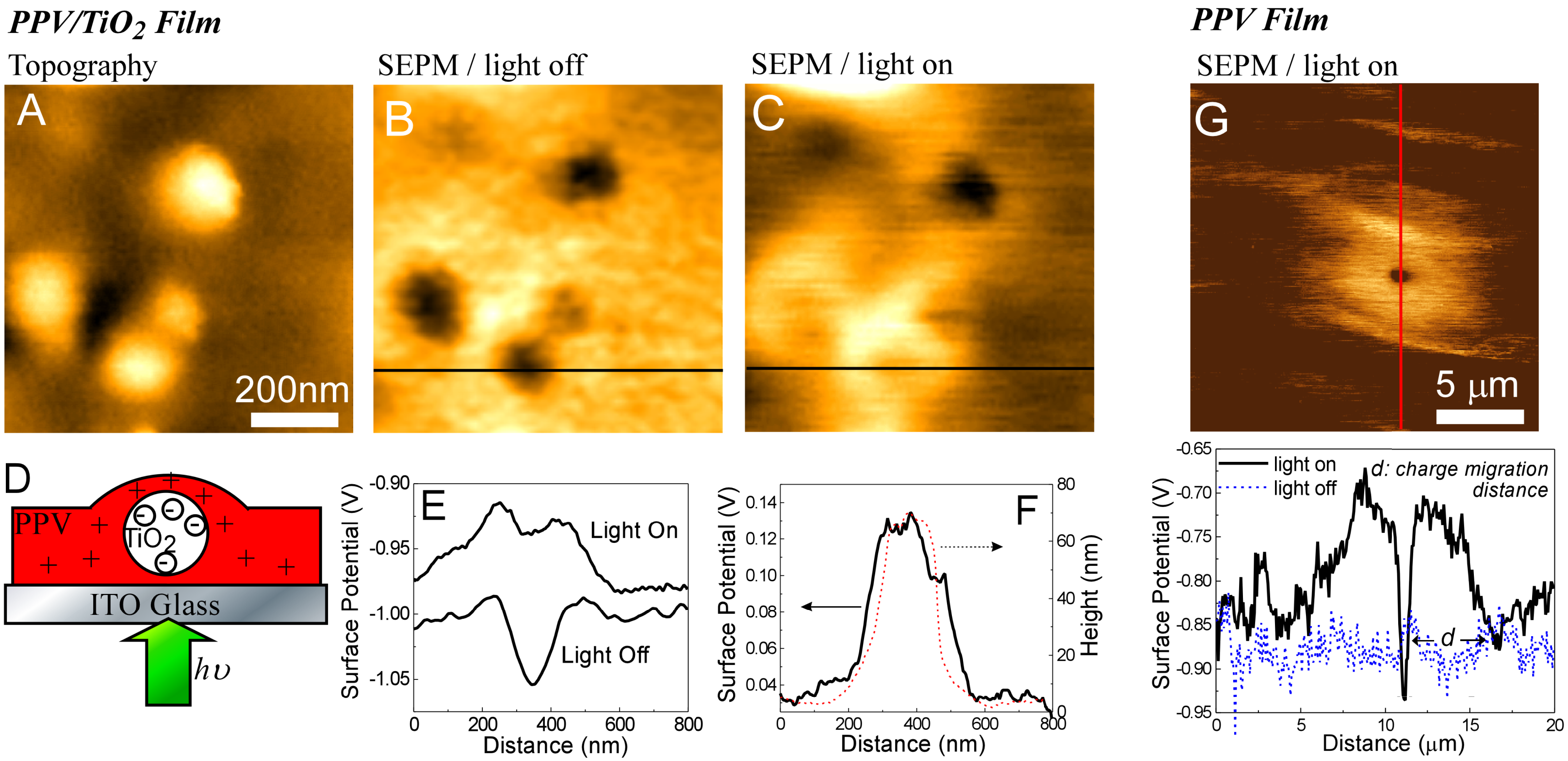
When applied bias V_b = - φ, all electrostatic interactions are nullified.

- *C* is the tip-sample capacitance;
- V_b is the bias voltage applied to the sample,
- φ is the surface potential difference between the tip and substrate,
- E_z is the static field due to charges or multipoles of the sample excluding the field of charges accumulated on capacitor plates, namely, the tip and the substrate under bias voltages.
- F_{VDW} is the van der Waals force,
- F_{hs} is the hard-sphere repulsion when the tip and the sample are in very close contact,

Typical applications of EFM

- characterizing surface electrical properties;
- electronic properties of nanocrystals (trap sites, charge storage, etc.);
- Interfacial charge transport and separation for organic/electrode devices (conducting polymer, organic semiconductors, etc.);
- detecting defects of an integrated circuit (silicon surface);
- measuring the distribution of a particular material on a composite surface.

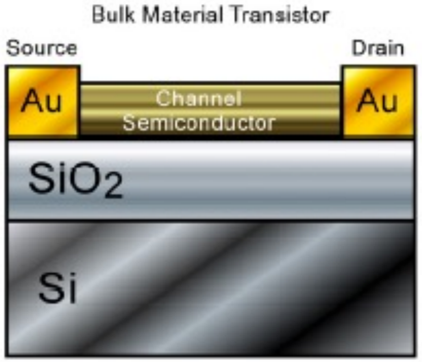
Example #1: Charge Migration in TiO_2/PPV Blends

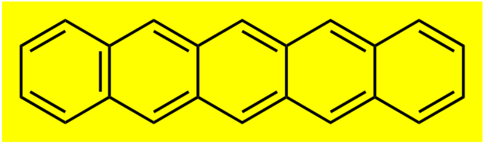


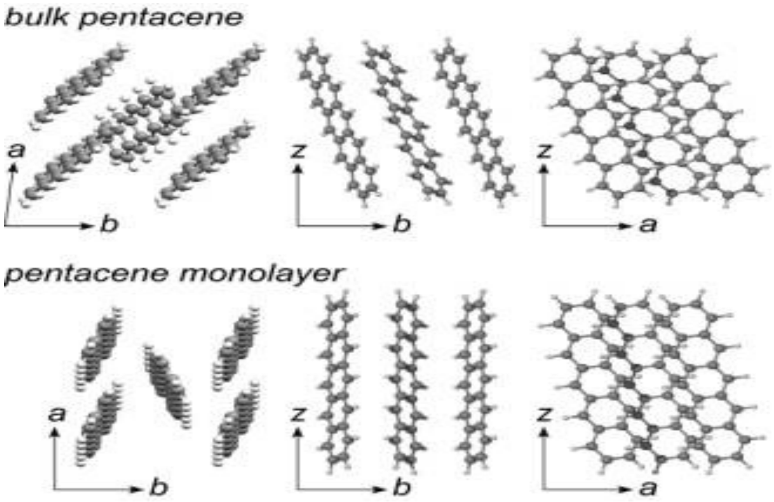
Liu, J. Phys. Chem. C 2009, 113, 9368–9374

Example #2: Charge re-distribution and Fermi level pinning at organic/inorganic interface

- For many organic semiconductors devices like TFT, LED, LCD, solar cells, interfacial charge transfer (electrode injection) represents the ultimate step in transport processes of charge carriers.
- The efficiency of interfacial charge transfer and/or separation determines the overall performance of the devices.
- EFM measurements provide direct mapping of the local charge density at high spatial resolution.
- Here the material used is pentacene, one of the most popular organic semiconductors, which has high charge mobility ~ 1 $cm^2\ V^{-1}\ s^{-1}$, and high gate modulation of current, $10^7 – 10^8$.







Liwei Chen, L. Brus, et al. J. Phys. Chem. B **2005,** *109,* 1834-1838

Pentacene on 25 nm SiO_2/Si (n-type)

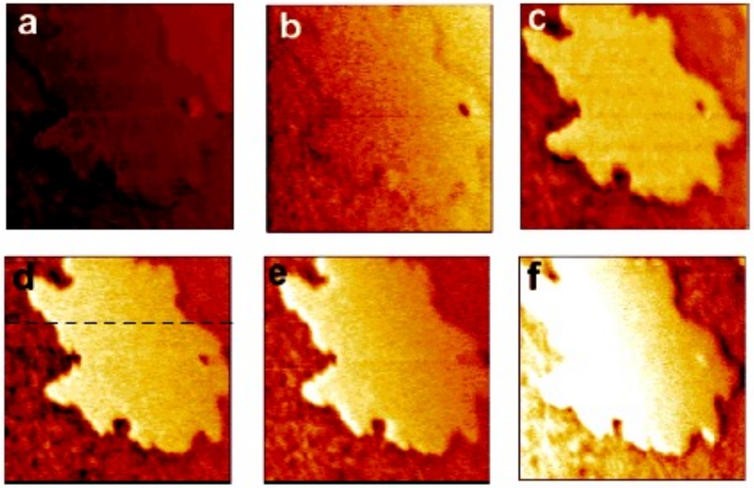


Figure 1. EFM images of pentacene islands on 25-nm SiO_2 at various bias voltage (a) −0.8 V (b) −0.6 V (c) −0.5 V (d) 0 (e) 0.2 V (f) 0.4 V. The scan size for all images is 800 nm.

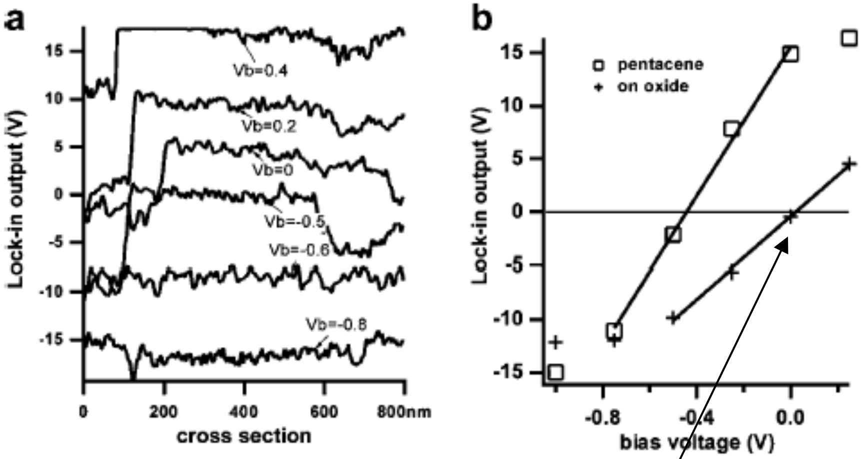


Figure 2. (a) Electric force profile across the pentacene island at the cross section labeled in Figure 1d. The offset in the pentacene island position is due to the scanner drift among the scans. (b) Electric force gradient averaged over a long time on pentacene and on silicon dioxide at various bias voltages.

Surface potential on pentacene is more positive than SiO2/Si
→ Interfacial charge separation

From the intersects, the potential difference between pentacene and SiO2 can be deduced, 0.5 V.

Liwei Chen, L. Brus, et al. J. Phys. Chem. B **2005,** *109,* 1834-1838

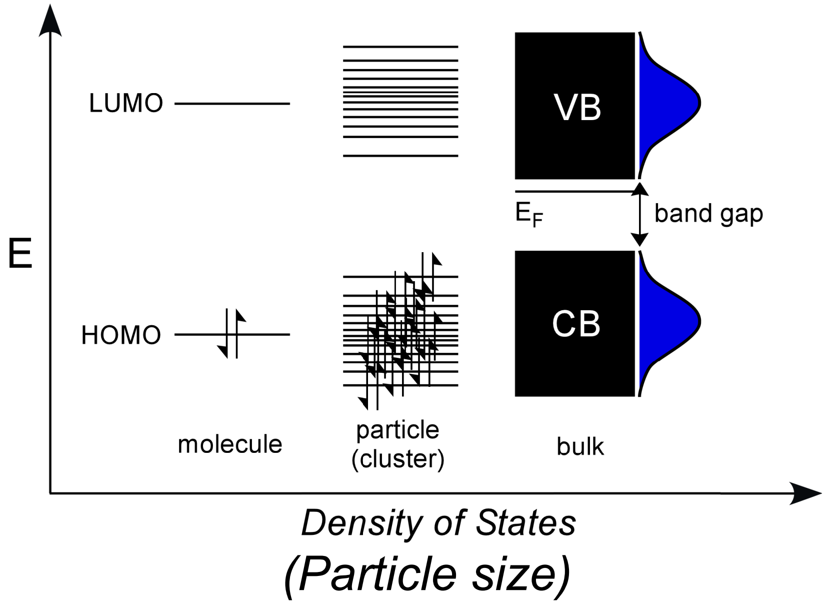
Example #3: Interfacial charge transfer of nanocrystals

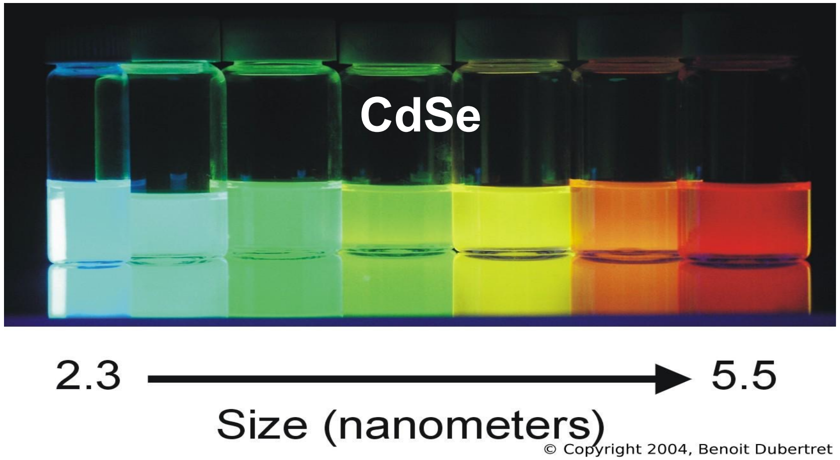
- Nanoparticle: a transition manifestation between molecules and bulk materials;
- Size-tunable physical and chemical properties;
- Large ratio of surface atoms --- defects density upon surface modification;
- Thus vast applications in optical and electronic devices;
- Interfacial charge transfer is crucial for understanding and designing nanocrystal based devices.

- *Detailed modeling and theoretical analysis of EFM measurement can be found in the following paper.*

Oksana Cherniavskaya, *L. Brus, et al. J. Phys. Chem. B* **2004,** *108,* 4946-4961

Tuning bandgap (i.e. λ_{em}): *Quantum Size Effect*





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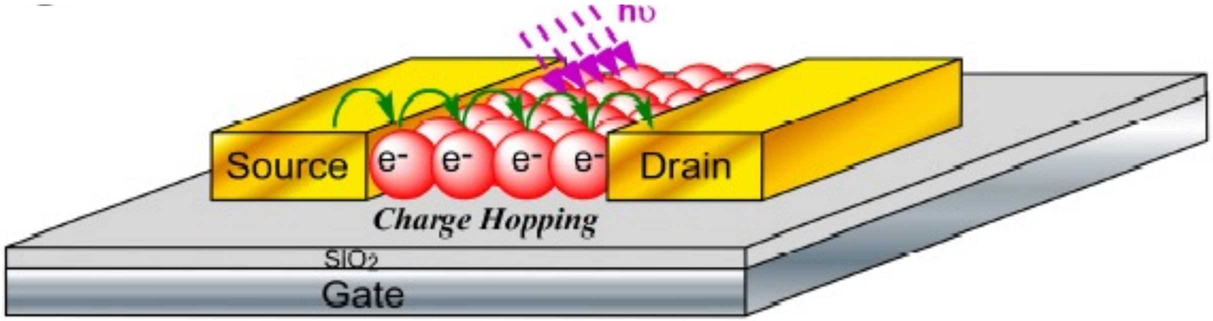
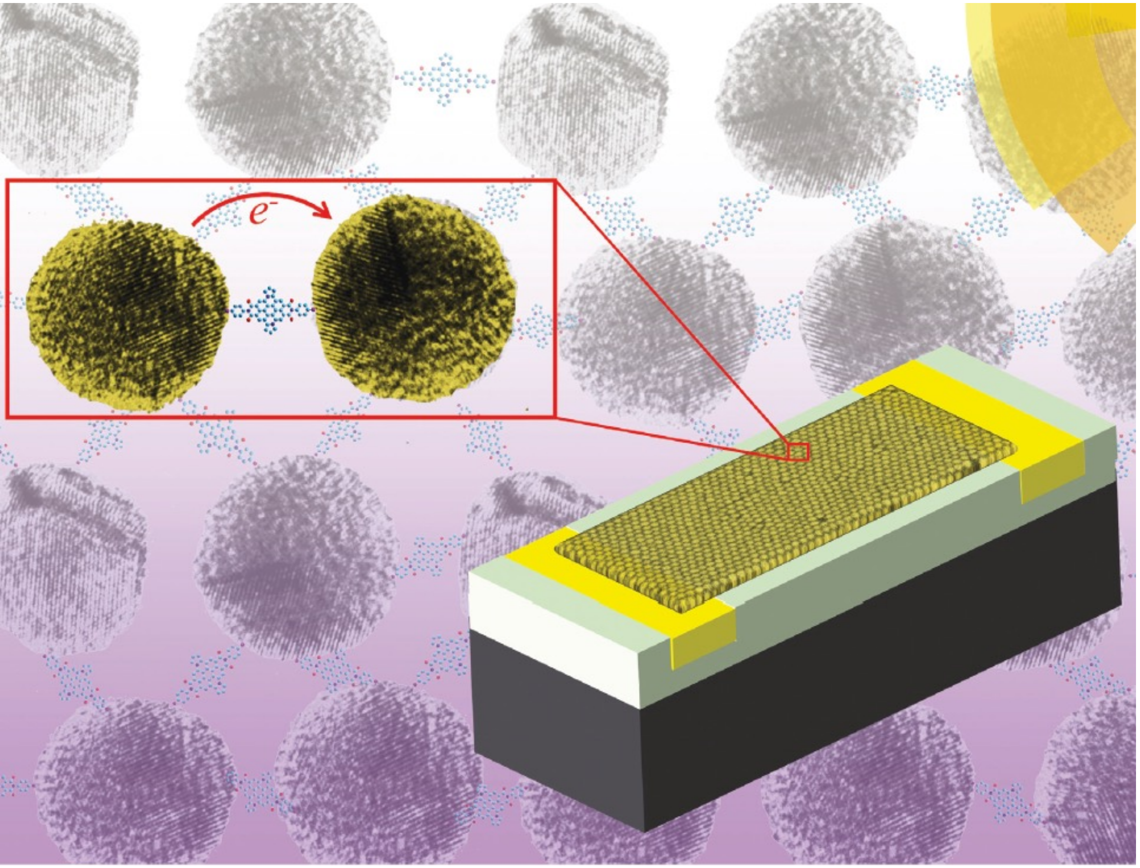
Thin-film transistor based on lateral assembly of nanocrystals

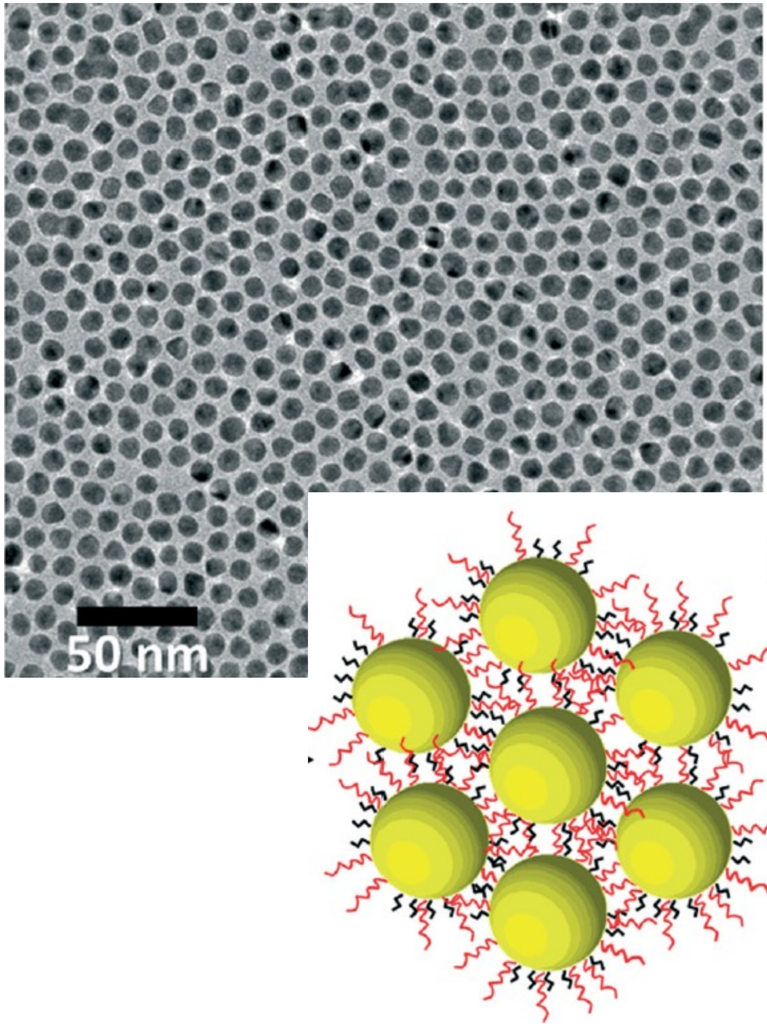


Electric-field directed 2D assembly of organic nanospheres:
Fabrication as TFT and optical switch devices.

Gate modulation results in depletion layer within the nanoparticles, i.e. formation of surface charges in surface layers.

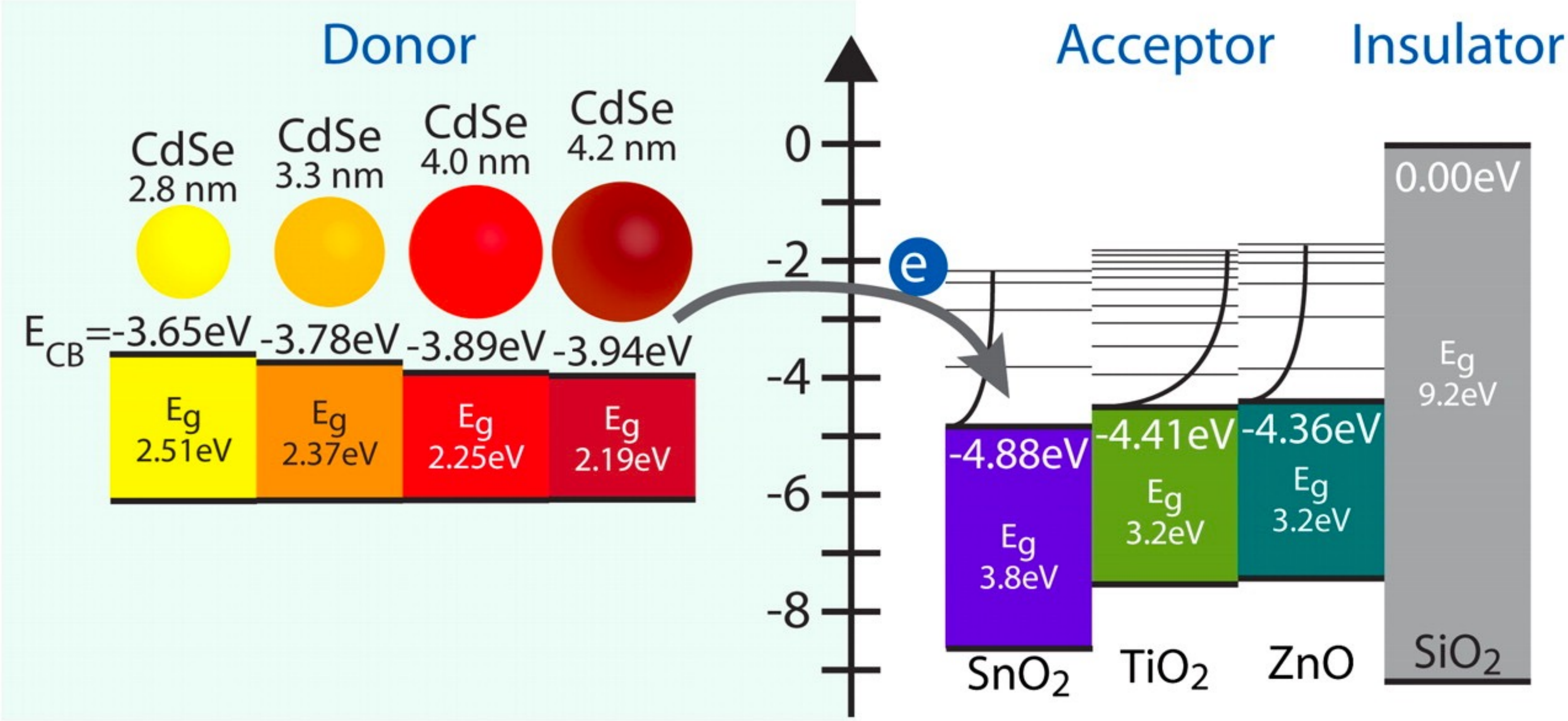
Electronics based on lateral assembly of nanocrystals





Zang and Hihath et al.,: *Mol. Syst. Des. Eng.*, 2017, 2, pp440

Example #3: Interfacial charge transfer of nanocrystals: EFM measurement



- Driving force of the electron transfer depends on the conduction band of QD, which in turn can be simply tuned by changing the particle size;
- Different driving force leads to different charge transfer kinetics and separation efficiency.

Example #3: Interfacial charge transfer of nanocrystals: EFM measurement

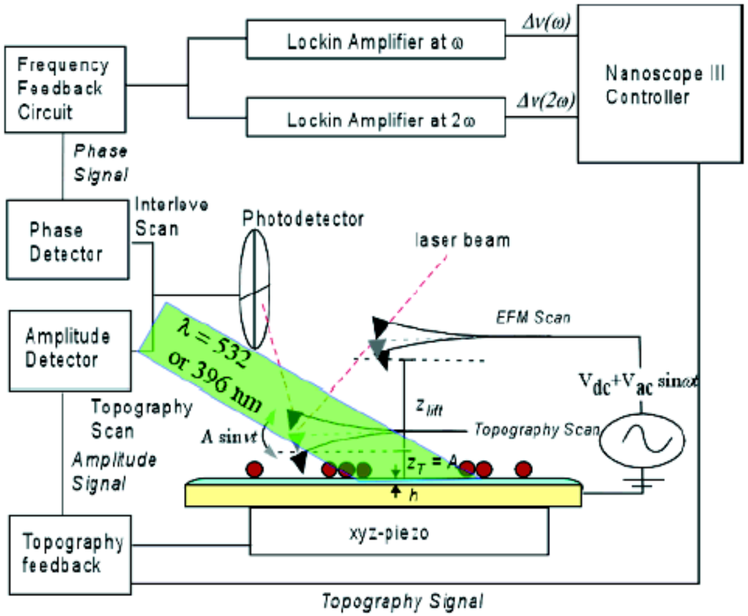
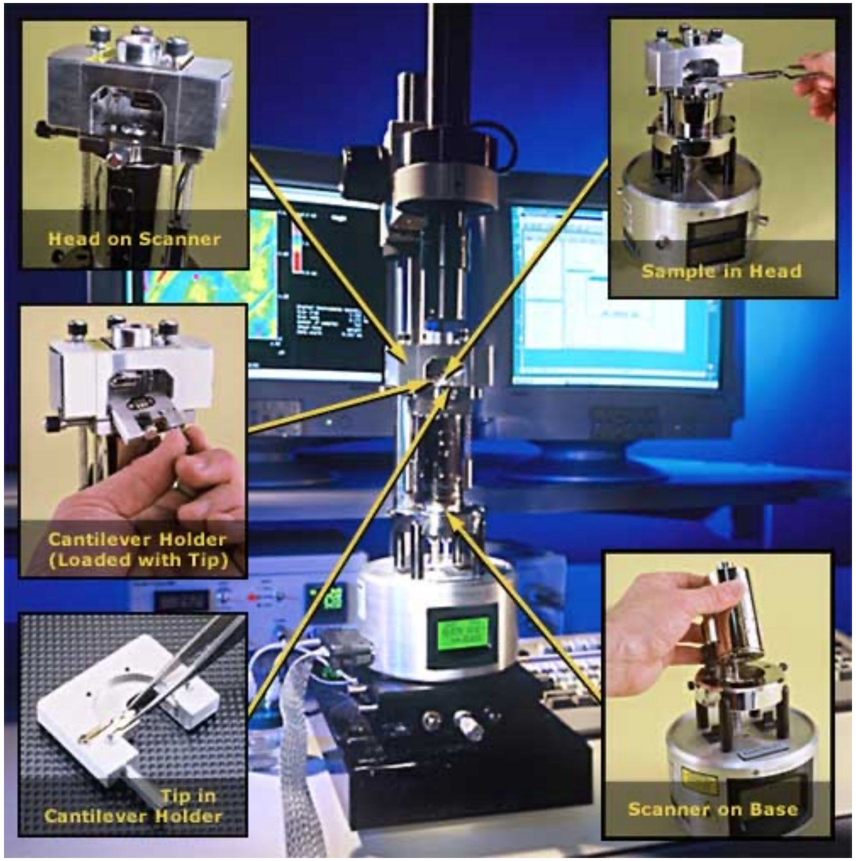
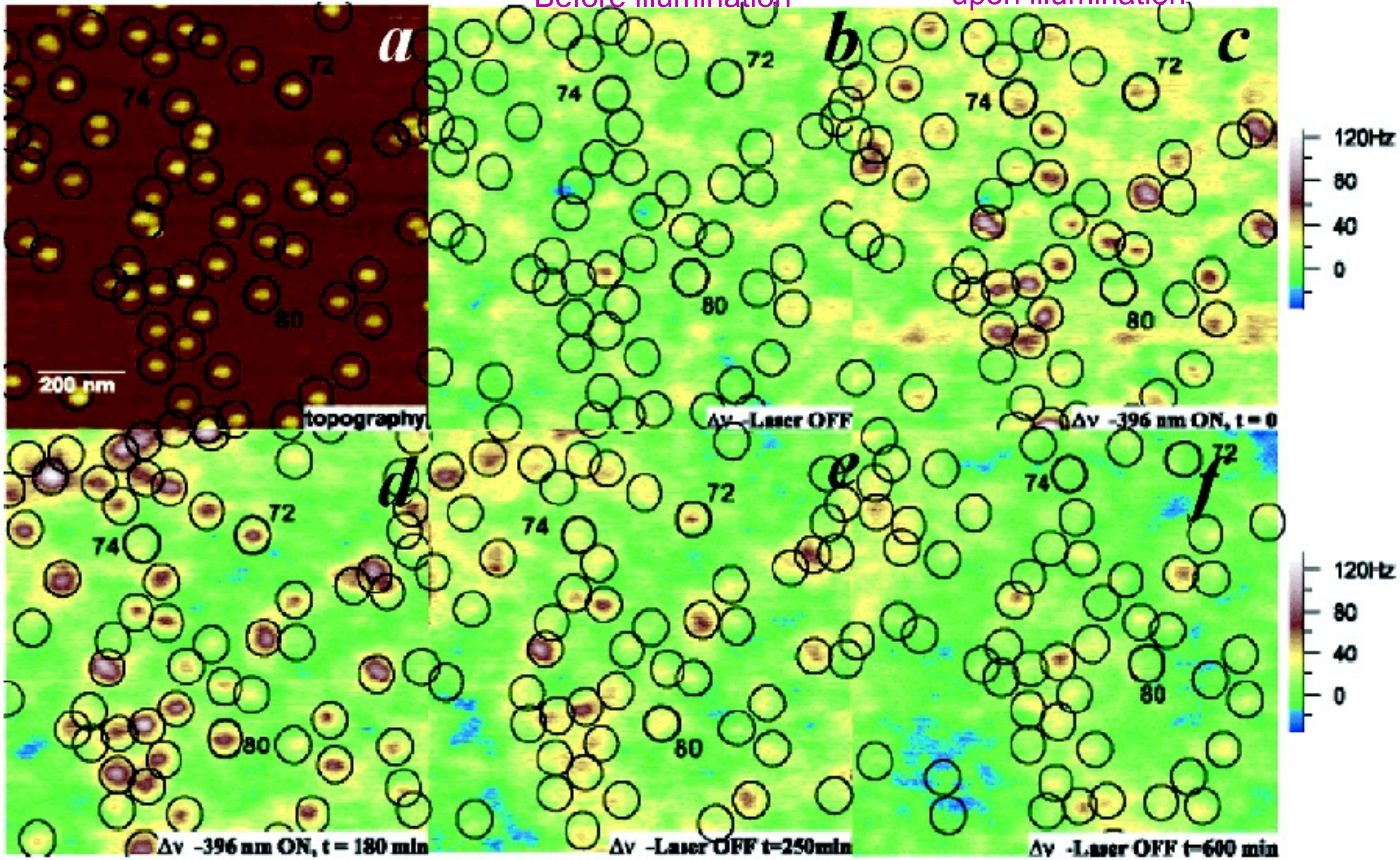


Figure 1. EFM experimental setup. The bottom portion of the flowchart shows that the tapping-mode topographic data is acquired on the first pass of a given line (main scan). The top of the chart represents the second scan of a given line (interleave scan), where the cantilever is lifted a set distance above the surface and scanned at constant height from the substrate while being dithered both mechanically and electrically. The frequency shift of the probe is detected by the phase-lock loop and fed into two external lock-in amplifiers, where the signals at frequencies ω and 2ω are isolated and fed back to the Nanoscope IIIa controller, where the image is created.



Oksana Cherniavskaya, *L. Brus, et al. J. Phys. Chem. B* **2004,** *108,* 4946-4961

CdSe/CdS nanocrystals on n-type silicon under illumination



Before illumination

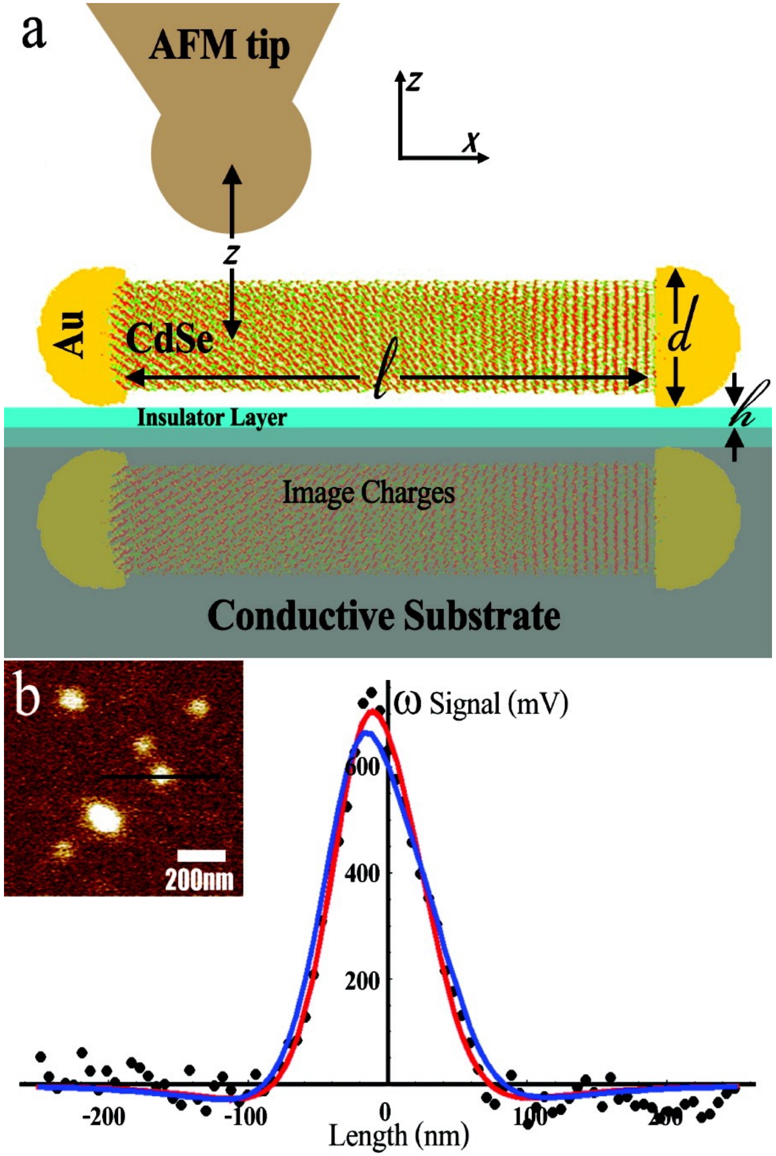
upon illumination

Figure 3. Topography (a) and charge (b−f) images of the same sample area of CdSe/CdS nanocrystals on N-type silicon with 12 Å, exposed to 396-nm photoexcitation. (b) Charge image prior to high-energy excitation; (c) first image taken once the laser is turned on; (d) image taken at t_{on} = 180 min; (e) image taken 250 min after the laser is turned off; (f) t_{off} = 600 min.

- Before exposure to light, there is only one nanoparticle showing a charge signal.
- Once exposed to light, many charged particles appear.
- Equilibrium is reached around 100 min.

J. Phys. Chem. B **2004,** *108,* 4946-4961

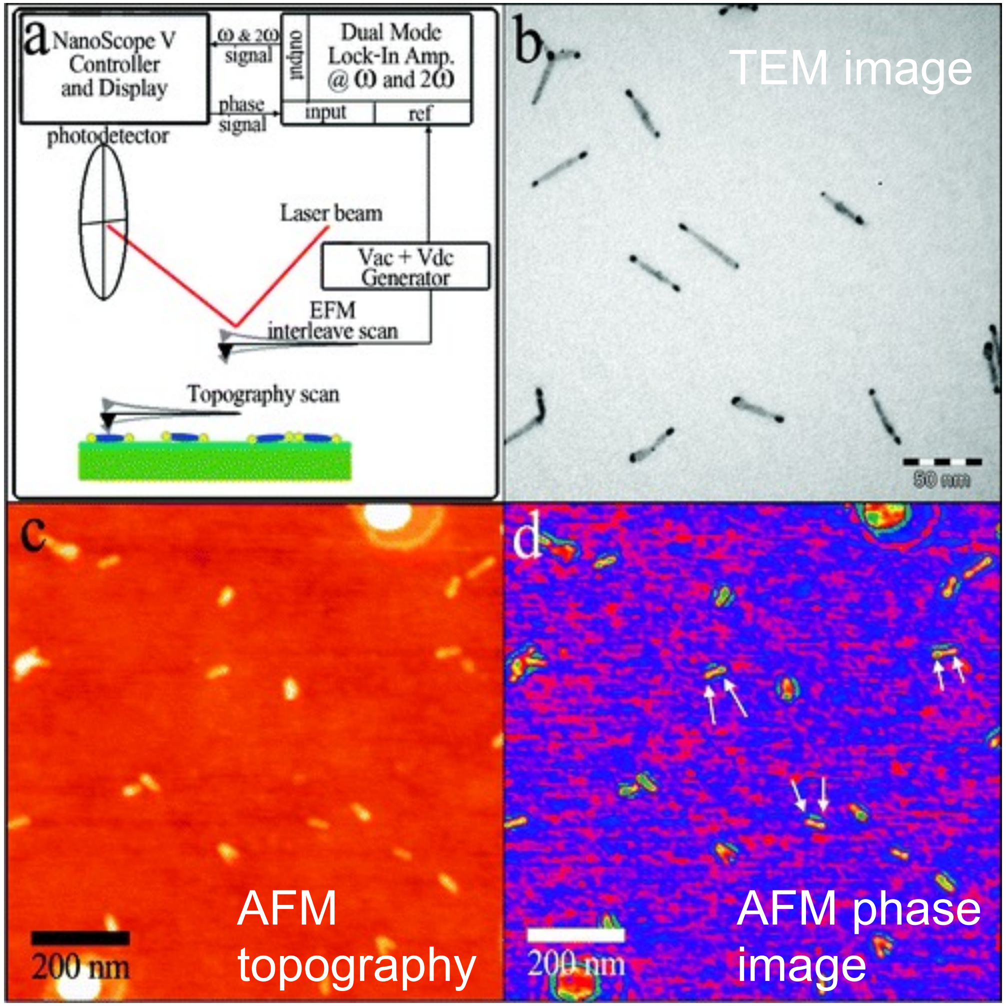
Example #4: Charge separation between semiconductor-metal nanoparticle: implication for a variety of applications in optoelectronic devices.



Electrostatic Force Microscopy Study of Single Au−CdSe Hybrid Nanodumbbells (NDBs): Evidence for Light-Induced Charge Separation

Nano Lett., 2009, 9 (5), pp 2031–2039

Example #4: Charge separation between semiconductor-metal nanoparticle: implication for a variety of applications in optoelectronic devices.

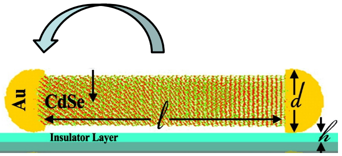


(a) A scheme of the EFM setup used demonstrating a two pass scan of each line with bias application in the interleaved scan. (b) TEM image of hybrid CdSe-Au nanodumbbells used in this work. (c) AFM tapping mode topography image of nanodumbbells with the corresponding phase image (d) showing contrast difference between the gold tips (white arrows) and the CdSe rods.

Example #4: Charge separation between semiconductor-metal nanoparticle: implication for a variety of applications in optoelectronic devices.

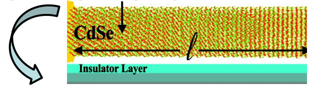
Nano-dumbbells

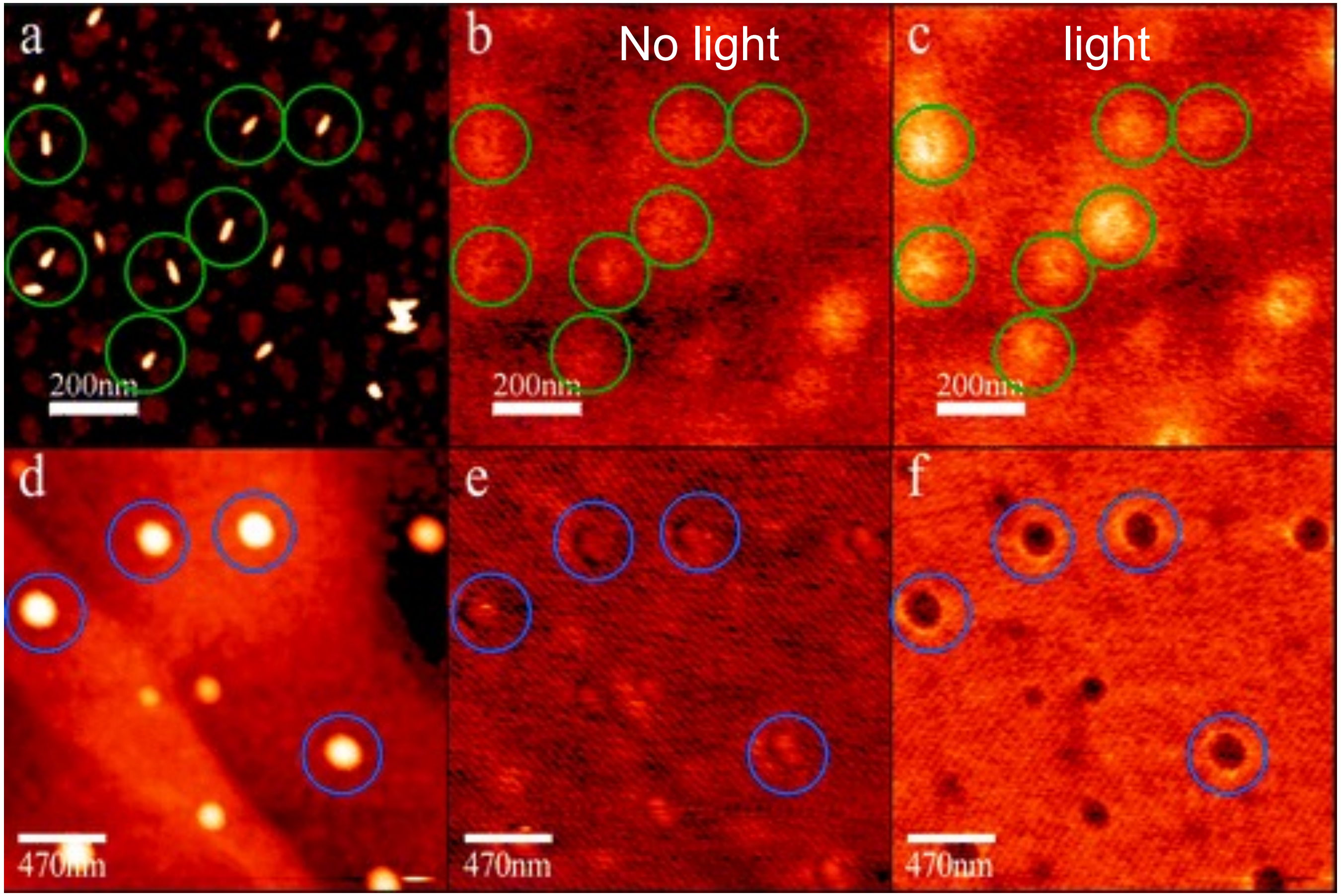
e-transfer



CdSe nanorods

e-transfer





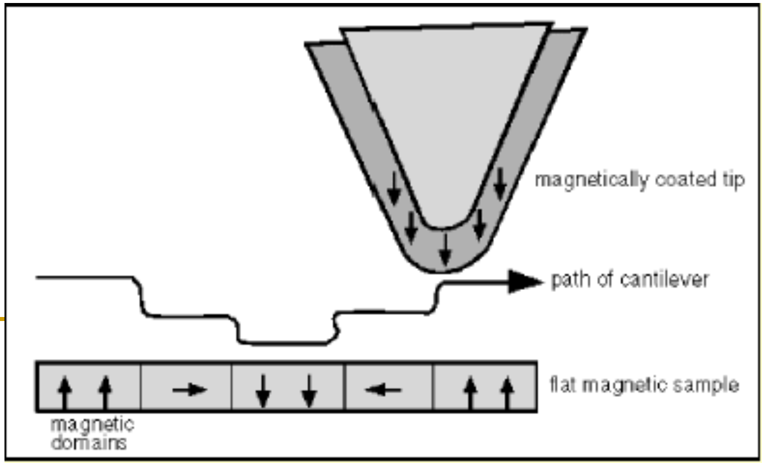
negative charge

Positive charge

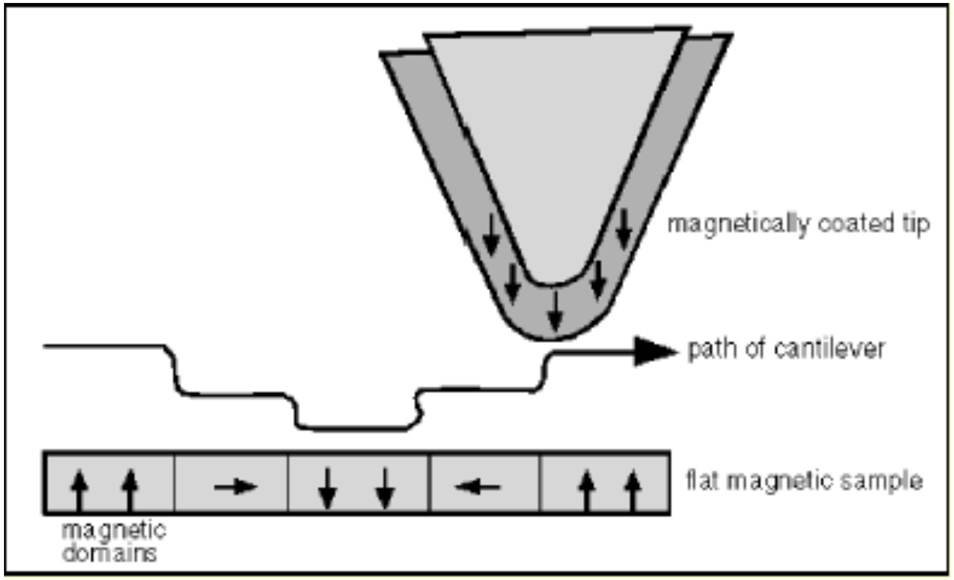
Correlated tapping mode topography image (a) and charge images (ω) before (b) and during (c) irradiation of a sample of NDBs. The change in the signal between images b and c is indicative of negative charging of the NDBs while under irradiation. In comparison, a correlated tapping mode topography image (d) and charge images (ω) before (e) and during (f) irradiation of a sample of CdSe nanorods shows a positive charging behavior under irradiation. (Circles on some of the particles are shown as a guide to the eye).

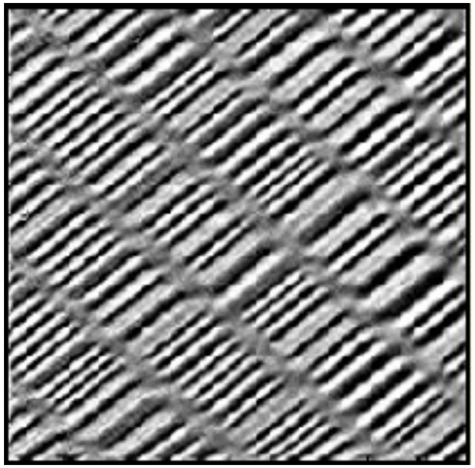
What is MFM?

- MFM is a secondary imaging mode derived from Tapping-Mode AFM.
- MFM images the spatial variation of magnetic field within the sample surface, through measuring local magnetic interaction between a conductive tip and a sample .
- In MFM, a magnetic tip coated with a ferromagnetic thin film (e.g., CoCr or NiFe) is used.
- MFM detects changes in the resonant frequency of the cantilever induced by the magnetic interaction with the sample surface.
- The cantilever’s resonance frequency and phase change with the strength of the magnetic field gradient and are used to construct the MFM image.
- MFM can be used to image both naturally occurring and deliberately written domain structures in magnetic materials.



Magnetic Force Microscopy (MFM)



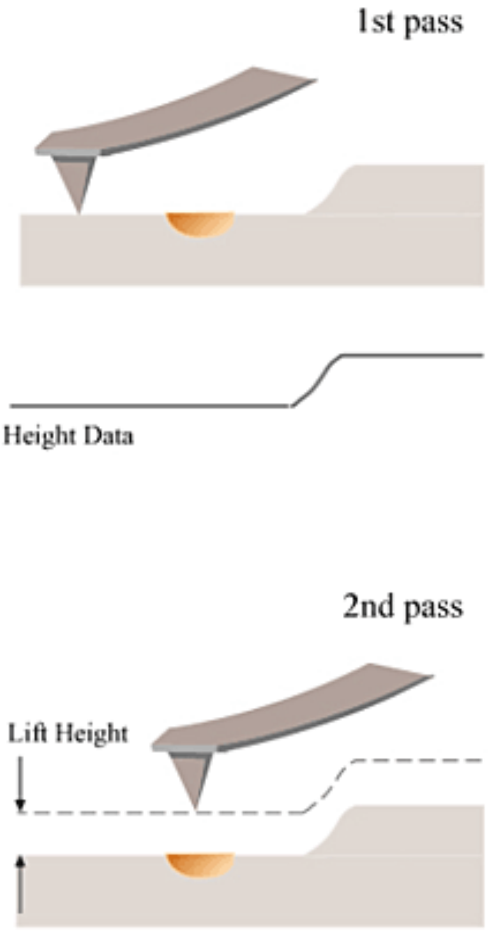


MFM image of a hard disk (30 μm)

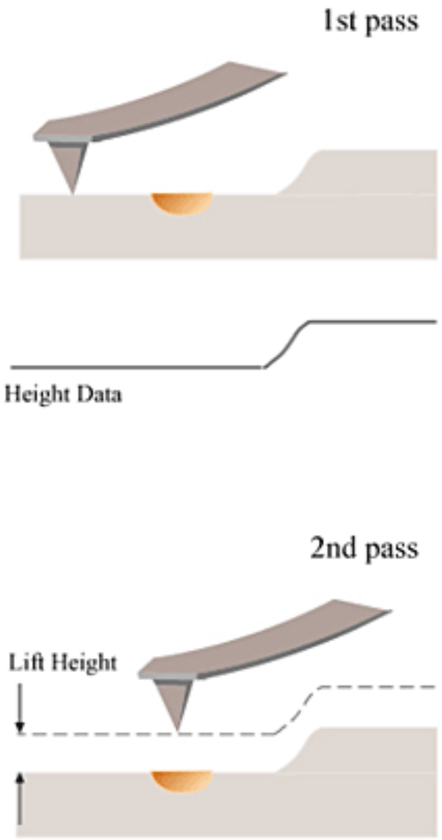
Dual scanning --- Lifted mode:

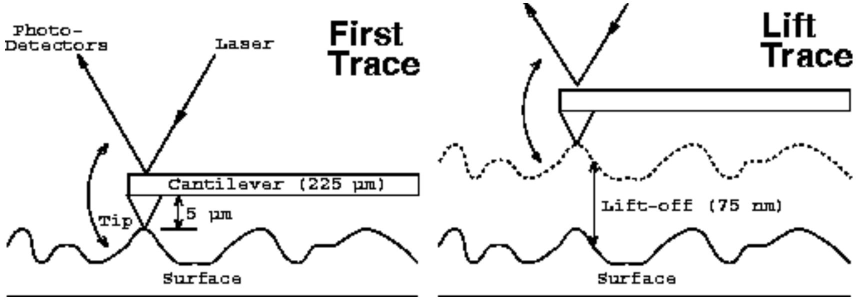
Lift-Mode --- a patented technique of DI. It separately measures topography and another selected property, like magnetic force (MFM), and electric force (EFM), using the topographical information to track the probe tip at a constant height (Lift Height) above the sample surface during the second scanning.

- Because the magnetic forces interact at greater distances than van der Waals forces, so electrical or magnetic force information can be separated from surface topography simply by increaseing the tip-to-sample distance --- lift up the tip.
- Dual scanning --- the tip first acquires surface topography in the tapping mode, then the tip is lifted up, and retraces the surface profile maintaining **constant tip-surface distance**.
- During the second scan, tip is no longer driven mechanically by the piezoactuator --- no feedback required.
- As the tip moves over an magnetic field gradient, it is either pulled toward or repulsed away from the sample, depending on the magnetic moment direction of the sample.
- The deflection (or frequency change) of the cantilever, proportional to the magnetic field strength, can be measured using the standard light-lever system.



Lifted-mode scanning





Applications and advantages of MFM imaging

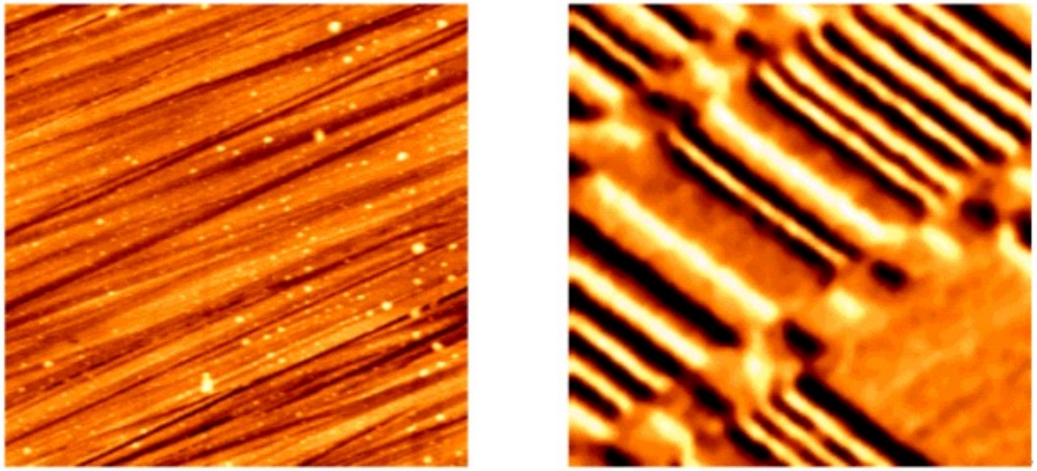
- MFM can be used to evaluate magnetic materials and devices or to locate and map magnetic defects on a variety of materials and surfaces.
- Applications of MFM imaging include:

1. data recording/storage media,
2. nanoparticles (e.g. biological separation and purification),
3. thin films,
4. detection of magnetic beads,
5. biological magnetic sensing (e.g. long migration of sea turtle and homing pigeon, next slide)

- MFM brings the advantages of AFM into the magnetic materials.
- MFM is non-destructive and requires minimal sample preparation.
- MFM is compatible with imaging in fluids or in air, imaging under controlled environments (e.g. pressure, temperature).

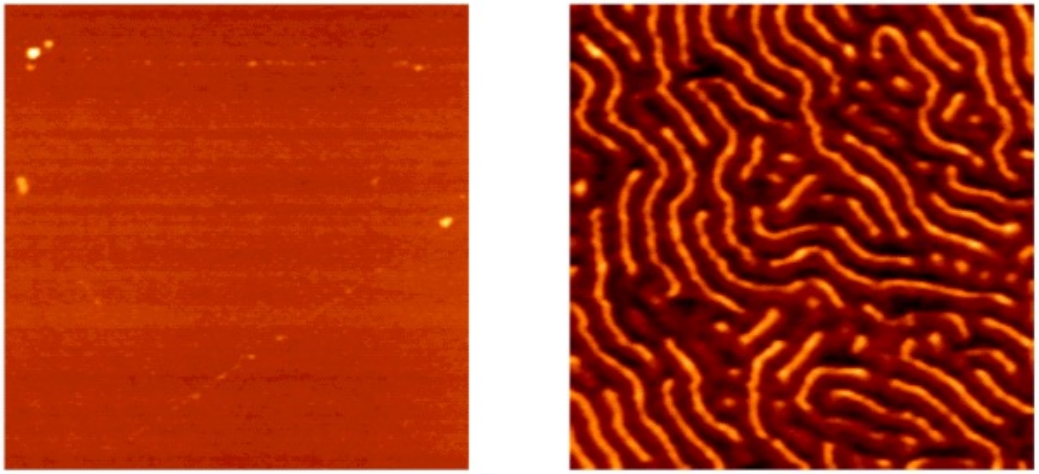
Example #1: revealing nanoscale magnetic domain

Hard disk



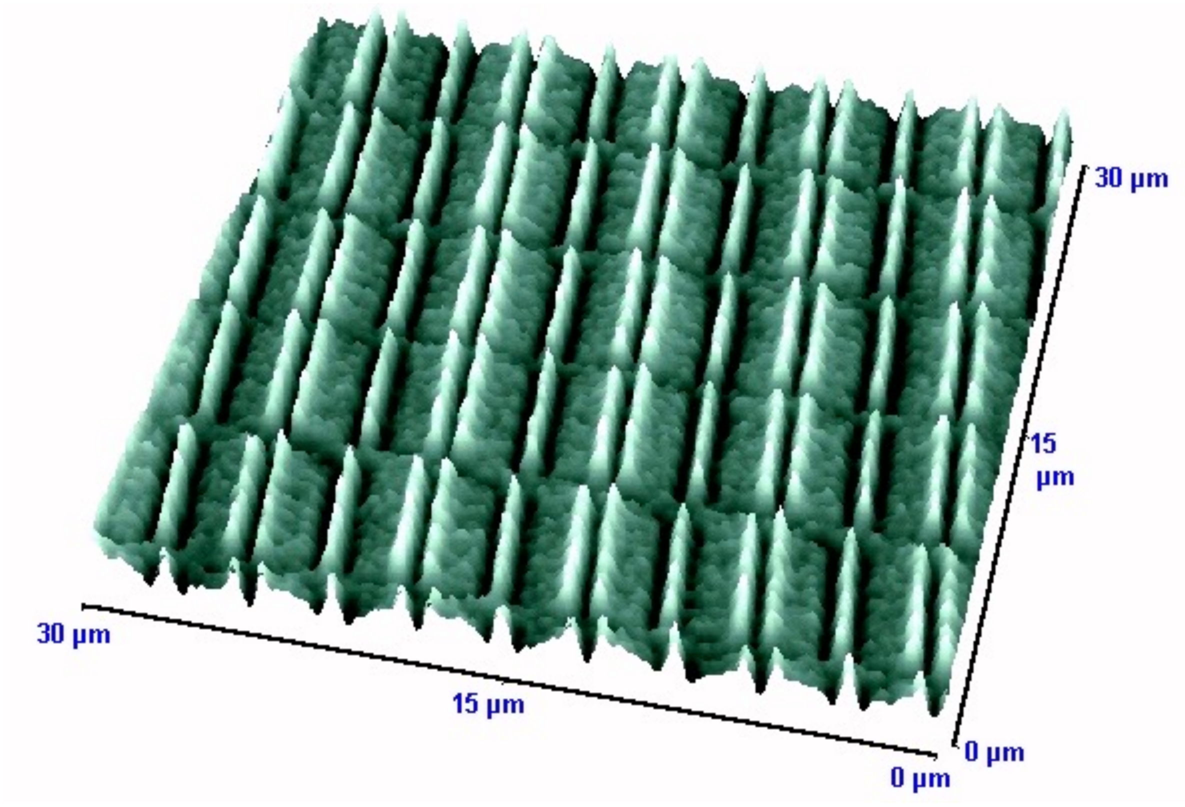
AFM **MFM**

(Ni-Fe_2nm/Au_3nm/Co_0.6nm)x11



AFM **MFM**

Example #2: Fabrication of New Generation of Hard Disk



Magnetic Force Microscopy (MFM) of a Magnetic Hard Disk

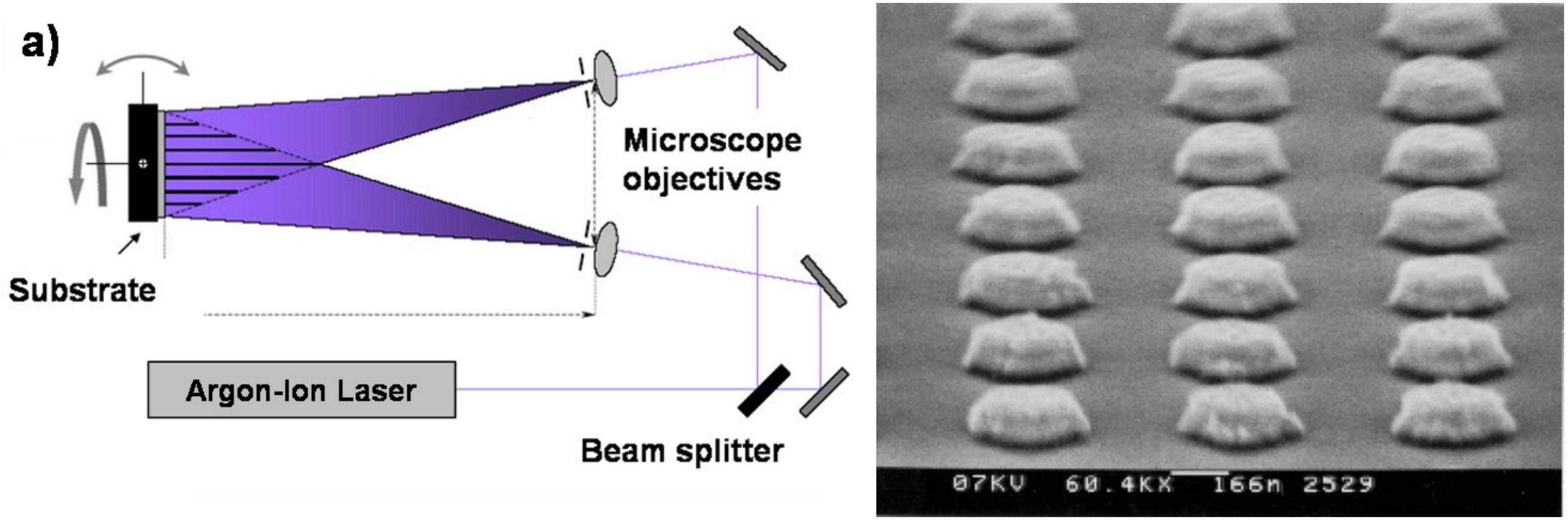
Mesoscopic structure of hard disk

- Conventional hard disks consist of sputtered magnetic thin films with single domain grains.
- The orientation of the magnetisation of these grains is randomly distributed in the plane of the medium.
- Some 100 grains are necessary to build one bit with a sufficient signal to noise ratio (S/N). The lateral size of a grain is typical 10 nm. Therefore the smallest allowable bit size is of the order of 100 x 100 nm^2.
- The grain size may be reduced, but for grain sizes smaller than 7 nm the magnetisation of one grain will become thermal unstable (superparamagnetic).
- In summary, the storage density in conventional hard disk is therefore fundamentally limited.

New generation of hard disk

- A solution to break the density limit of conventional hard disk --- to pattern the magnetic layer in a regular matrix of dots.
- In such a discrete recording medium, every dot represents one bit.
- One requirement --- these dots are single domain and have a strong uniaxial magnetic anisotropy, so that only two well defined magnetisation states are possible.
- It is obvious that a special patterning technique is required --- a large and regularly patterned area of at least 50x50 nm^2 sized dots with 100 nm period can be obtained. See the slide.
- Also, for the recording of this type of media, new technologies have to be developed.

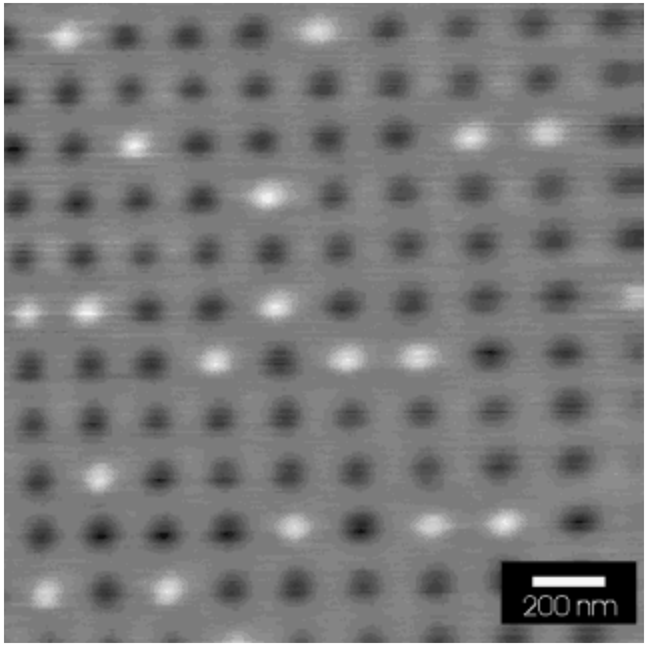
Laser Interference Lithography



Working principle of laser interference lithography, and examples of etched dot structure patterned with Laser Interference Lithography (period = 570 nm)

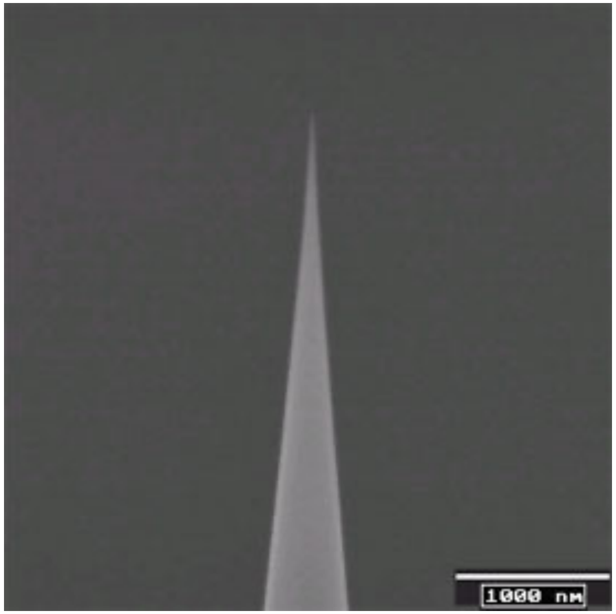
M.A.M. Haast et al., *Journal of Magnetism and Magnetic Materials Vol. 193 1999 511-514*

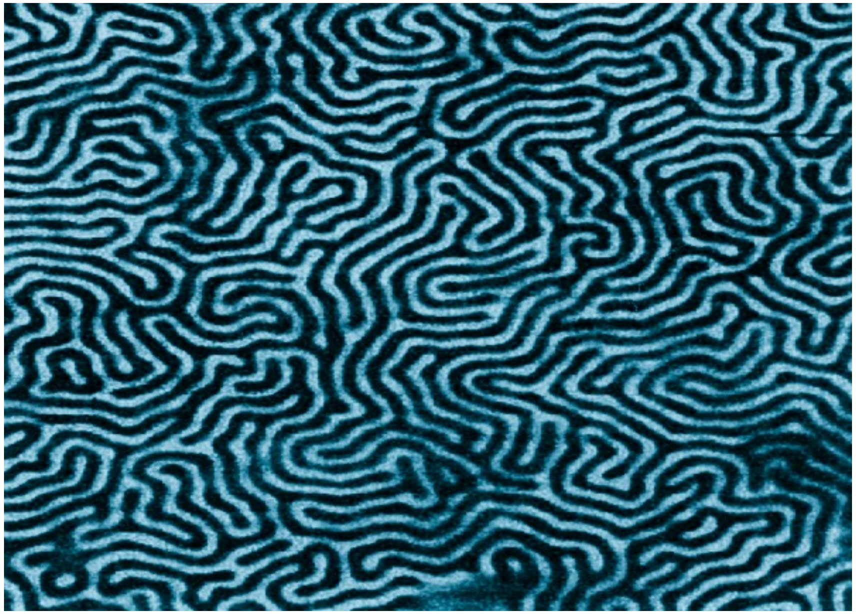
Magnetic Force Microscopy image of 70 nm single domain dots at 200 nm period



- The dots are in a single domain state with only two orientations, i.e. up and down;
- This meets the requirement for a patterned medium.
- The density of this medium is 16 GBit/In^2, considerably higher than state-of-the-art hard disk technology. --- remember this was in 1999.

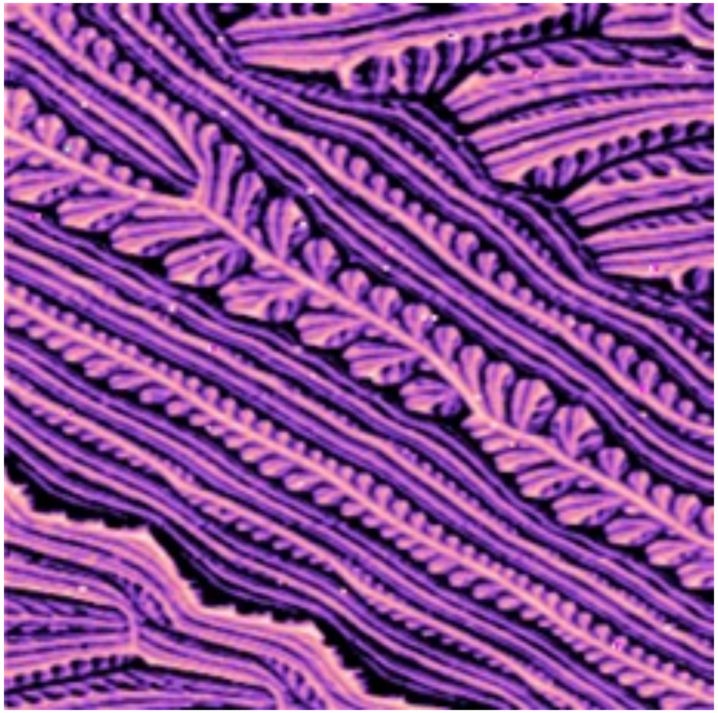
Example #3 : High lateral resolution using sharp tip





(10 µm x 10µm) Magnetic Force Microscope scan of a 200nm thick cobalt crystal layer showing magnetic domains

Example #4 : inhomogeneous magnetic domain in atomic homogeneous phase



Magnetic Force Microscopy image of a (111) surface of a Fe 3%Si single crystal, displaying a multi-scale domain structure (40x40µm²).

Case study #1: Navigation in the Sky

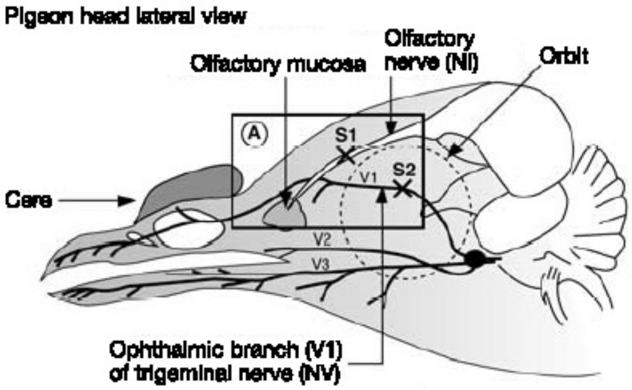
Homing pigeons can find their way home with ease.

Pigeons Detect Magnetic Fields, *knowing North (and South, West and East)*

Researches showed:

Bird beaks contain small magnetic particles called *magnetite*.

Using magnetite, the birds are able to sense the Earth's magnetic fields that provide information about location.



Nature, 2004, vol.432, pp508-511.

Magnetoreception and its trigeminal mediation in the homing pigeon

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INTERFACE

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Review

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Magnetoreception in birds

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Birds can use two kinds of information from the geomagnetic field for navigation: the direction of the field lines as a compass and probably magnetic intensity as a component of the navigational 'map'. The direction of the magnetic field appears to be sensed via radical pair processes in the eyes, with the crucial radical pairs formed by cryptochrome. It is transmitted by the optic nerve to the brain, where parts of the visual system seem to process the respective information. Magnetic intensity appears to be perceived by magnetite-based receptors in the beak region; the information is transmitted by the ophthalmic branch of the trigeminal nerve to the trigeminal ganglion and the trigeminal brainstem nuclei. Yet in spite of considerable progress in recent years, many details are still unclear, among them details of the radical pair processes and their transformation into a nervous signal, the precise location of the magnetite-based receptors and the centres in the brain where magnetic information is combined with other navigational information for the navigational processes.

1. Introduction

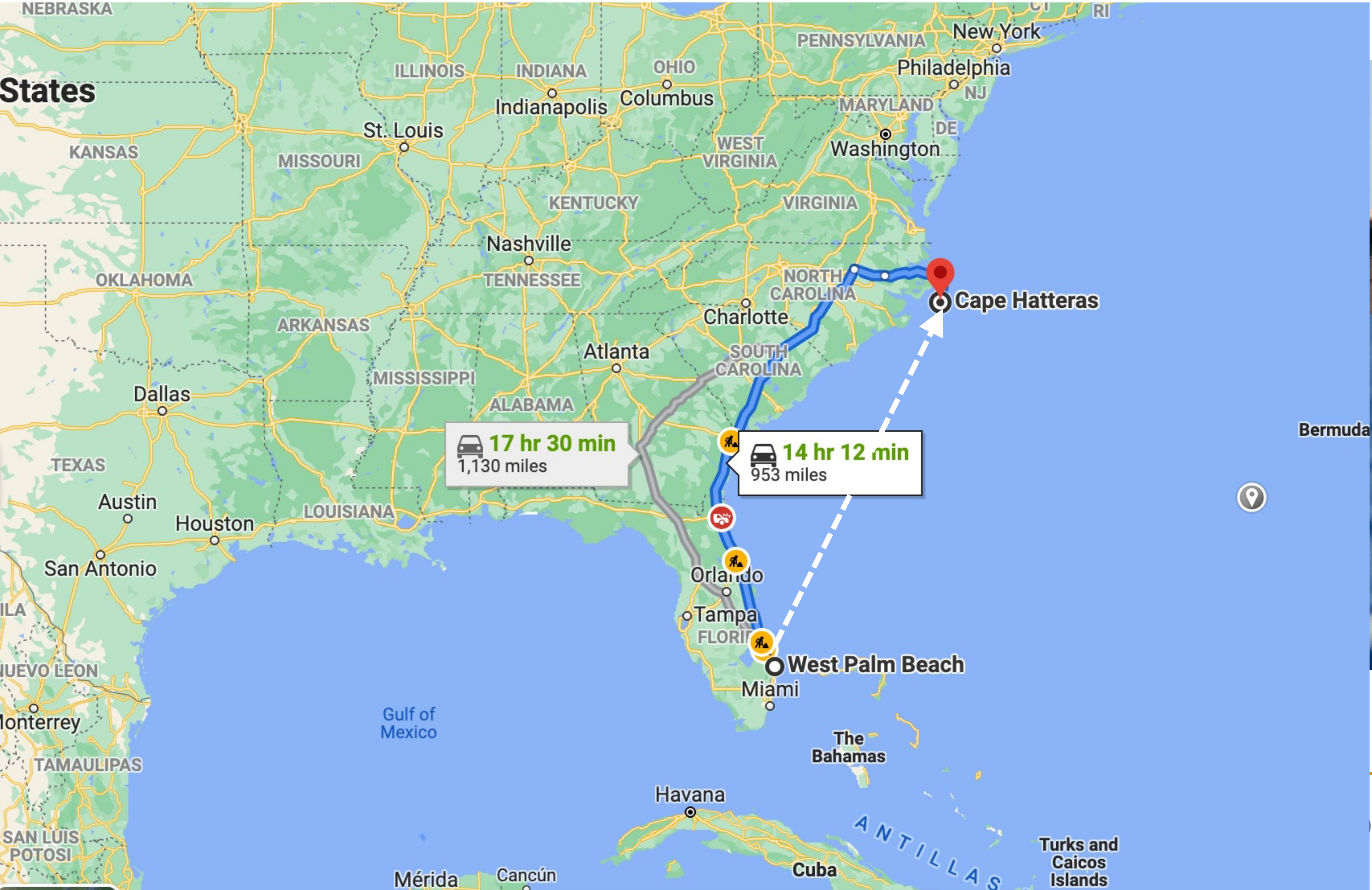
The magnetic field of the Earth provides animals that can sense it with navigational information: the vector indicates directions, and magnetic intensity and inclination, which decreases from the magnetic poles to the magnetic equator, and possibly also magnetic declination could be used as components of the

Case study #2: Navigation under the dark water, in the ocean (nanoscopic magnetic sensor? --- *to be explored by MFM*?)


Photo credit: UCF Turtle Group

- As hatchlings, turtles that have never before been in the ocean are able to establish unerring courses towards the open sea and then maintain their headings cross the ocean;
- homing back to specific locations after long migrations.

“We were surprised by how quickly the turtles traveled and how far they traveled,” says Mansfield. For example, one turtle took only 11 days to make it from West Palm Beach, Florida, to Cape Hatteras, North Carolina—a roughly 700-mile trip when you factor in the turtle’s floating route, Mansfield estimates.



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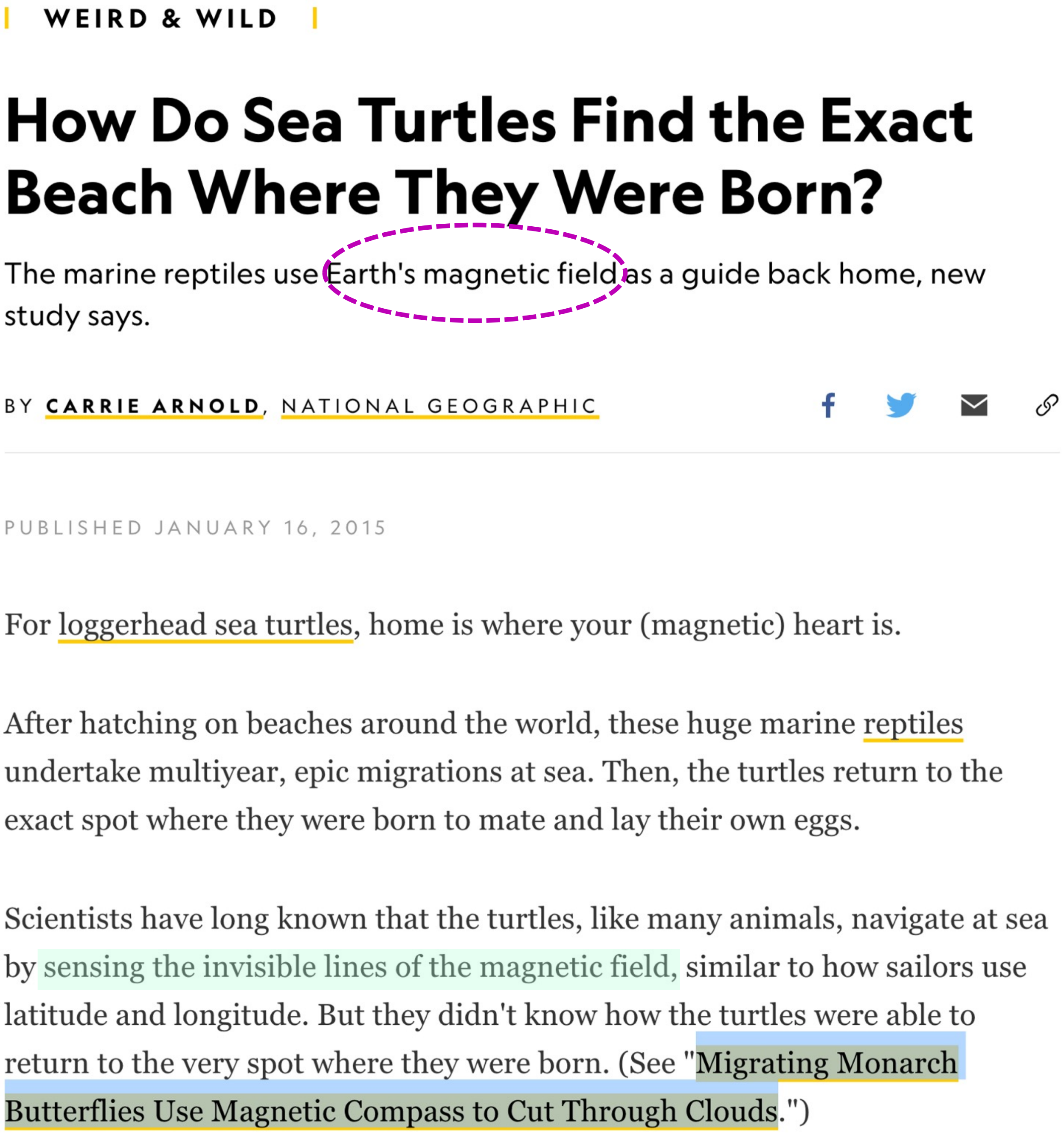

WEIRD & WILD

How Do Sea Turtles Find the Exact Beach Where They Were Born?

The marine reptiles use Earth's magnetic field as a guide back home, new study says.

BY **CARRIE ARNOLD**, NATIONAL GEOGRAPHIC

PUBLISHED JANUARY 16, 2015

For loggerhead sea turtles, home is where your (magnetic) heart is.

After hatching on beaches around the world, these huge marine reptiles undertake multiyear, epic migrations at sea. Then, the turtles return to the exact spot where they were born to mate and lay their own eggs.

Scientists have long known that the turtles, like many animals, navigate at sea by sensing the invisible lines of the magnetic field, similar to how sailors use latitude and longitude. But they didn't know how the turtles were able to return to the very spot where they were born. (See "Migrating Monarch Butterflies Use Magnetic Compass to Cut Through Clouds.")

Migrating Monarch Butterflies Use Magnetic Compass to Cut Through Clouds

New research finds that monarch butterflies use a magnetic compass on overcast days.

BY **JANE J. LEE**, NATIONAL GEOGRAPHIC

PUBLISHED JUNE 23, 2014

When monarch butterflies wing their way south to central Mexico each fall, they use the sun to ensure that they stay on course. But how they head in the right direction on cloudy days has been a mystery—until now.

It turns out they use Earth's magnetic field as a kind of backup navigational system.

It's not unusual for animals engaged in long-distance migrations, including sea turtles and birds, to use an internal magnetic compass to get to where they're going. But whether monarch butterflies have a similar ability had previously been unclear: Some studies had found weak evidence for a magnetic compass, while others found none at all. (Read about other great animal migrations.)