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Understanding Methods to Determine Energy Levels of Quantum Dot Films for Device Integration

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ABSTRACT

Knowing the energy levels in quantum dot films is a crucial variable for determining materials to be used for electrodes and other active layers (i.e., hole blocking layer, as well as operation conditions in quantum dot devices. Kelvin Probe Force Microscopy (KPFM), a technique commonly used to determine the contact potential difference between materials, is used to determine the Fermi level position of lead chalcogenide and silver chalcogenide quantum dot films. Choice of capping ligand during film formation is shown to have significant effect on the position of the Fermi level, valence, and conduction bands. In Ag_2Se quantum dots films a 0.3 eV variation in Fermi level as a function of capping ligand is observed while 0.45 eV variation is observed in PbSe quantum dot films, with iodide-based ligands showing the highest Fermi level position and oleylamine displaying the lowest. KPFM measurement procedure is outlined, and the current strength and limitations of the technique are discussed.

Keywords: KPFM, Quantum Dots, Fermi Level, Energy Levels,

1. INTRODUCTION

Optoelectronic device fabrication can be quite complex with many different variables affecting performance. The complexity of the problem grows even larger when working with nanoscale materials whose electronic properties can be greatly altered by the surface chemistry such as quantum dots (QDs). Previous reports have shown the surface chemistry such as capping ligand can shift the energy band positions by up to 1eV, even when working with quantum dots of the same size and material[1]. The ability to alter the electronic properties of QDs is considered one of the biggest advantages when it comes to device fabrication, allowing for the possibility of creating quantum funnels[2] and band alignment engineering to optimize device performance[3]. However, predicting the changes in band position that will occur is not trivial and often requires complex modeling and there are only a few methods to experimentally determine the band position.

There are several electronic properties that are of importance when fabricating an optoelectronic device, the first of which is the bandgap, which is defined as the gap between the valence band and conduction band. The optical band gap can be experimentally determined through absorption measurements which can then be added to Coulombic stabilization energy of the confined electron and hole to determine the transport bandgap[1], [4]. While this is an easy method to determine the gap between the valence and conduction band, it gives no information on where the energy levels lie in respect to vacuum. Determining the absolute energy levels of a semiconductor film is often accomplished by ultraviolet photoelectron spectroscopy(UPS)[1], [5], which measures the energy spectra of photoelectrons emitted by molecules which have absorbed ultraviolet photons. Combining UPS with absorption measurements is the most reliable method to determine valence band and Fermi level position as well as the bandgap. However, another technique that has been used successfully to determine the electronic properties at the nanoscale[6], [7], Kelvin probe force microscopy (KPFM), could also be potentially useful in determining the Fermi level of quantum dot films. KFM is an atomic force microscopy (AFM) technique that measures the surface potential of the sample via the electrostatic forces resulting from the interaction between a conductive AFM tip and sample. The measured surface potential can then be compared to materials of a known work function to determine the sample work function or Fermi level. Herein, we report KPFM measurements performed on PbSe and Ag_2Se QDs with various ligands and determine the QD film Fermi level using gold as a standard, we also assess whether the technique is appropriate for determining absolute work function levels or is better used as a comparative measure.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of PbSe and Ag_2Se QDs

PbSe QD synthesis: PbSe QDs were prepared via previously reported methods[8] which are briefly outlined here. First, 8 mmol of $PbBr_2$ was added into a three-neck flask with 9 mL of oleylamine (OLA) and 16 mL of octadecene (ODE), the solution was degassed at 100°C for 2 hours while being magnetically stirred. After degassing the three-neck flask was switched to an N2 atmosphere, 1 mL of 2M tri-octylphosphine selenide (TOPSe), 2 mL of OLA, and 0.1 mL of di-i-butylphosphine were swiftly injected into the Pb-solution at 120°C, the flask was immediately removed from heat and allowed to cool to room temperature. QD purification was performed by washing with a mixture of chloroform ($CHCl_3$) and acetonitrile (ACN) followed by centrifugation and redispersal in $CHCl_3$ 3 times, after the third wash QDs were dispersed in hexane, allowed to sit overnight, and centrifuged again in the morning to remove any unreacted $PbBr_2$. An in-solution ligand exchange was then performed by dispersing 100-200 mg of the desired ligand in 5 mL N-dimethylformamide (DMF), followed by the addition of 5 ml (roughly 10mg/mL concentration) of QD solution in hexane on top of the DMF-ligand solution. Agitation of the ligand and QD phase separated solution resulted in the transfer of QDs from the hexane phase to the DMF phase, after which the hexane phase was discarded. To purify the newly capped QDs 5 mL of $CHCl_3$ was added to the QD/DMF solution and the mixture was centrifuged causing the QDs to crash out. The QDs were then redispersed in 2.5 mL of 2,6-diflouropyridine, at this point the QDs were ready for film preparation.

Ag_2Se QD synthesis: Ag_2Se QDs were also prepared via previously reported methods[9] which are briefly outlined here. First, 2 grams of $AgNO_3$ and 40 mL of OLA were added to a three-neck flask and degassed at 100°C for 2 hours while being magnetically stirred. After degassing, the flask was put under N2 atmosphere and 6 mL of 1M TOPSe was inject into the solution, the reaction was allowed to carry out at 100°C for 6 minutes. After 6 minutes, the reaction was clenched with a water bath and QDs were purified 3 times with $CHCl_3$ and ACN. After purification, QDs were dispersed in 10 mL of hexane.

Absorption spectra of both PbSe and Ag_2Se QDs can be seen in figure **1**.

2.2 Preparation of QD films for KPFM measurement

Conductive substrates are required to perform KPFM measurements, therefore we utilized Si/SiO_2 wafers with 200 nm of gold evaporated onto the surface. PbSe QD films were prepared by spincoating followed by a 10-minute annealing step at 90°C. Ag_2Se QD films were also prepared by spincoating, but solid-state ligand exchange was performed to replace OLA ligands. Solid-state ligand exchange was accomplished by spincoating QD solution followed by 5 second submersion of QD film in a 0.2M solution of ligand in methanol which was followed by three cleaning steps in which QD film was submerged in pure methanol.

Preparation of films for measurement was accomplished by removing a small amount of QD film from the edge of the substrate to expose the gold surface. Silver paste was used to electrically connect the QD film/gold substrate to the sample holder (see figure **1**). KPFM measurements were performed using the PeakForce KPFM mode on a Bruker Dimension FastScan with Scanasyst AFM utilizing PFQNE AL AFM probes.

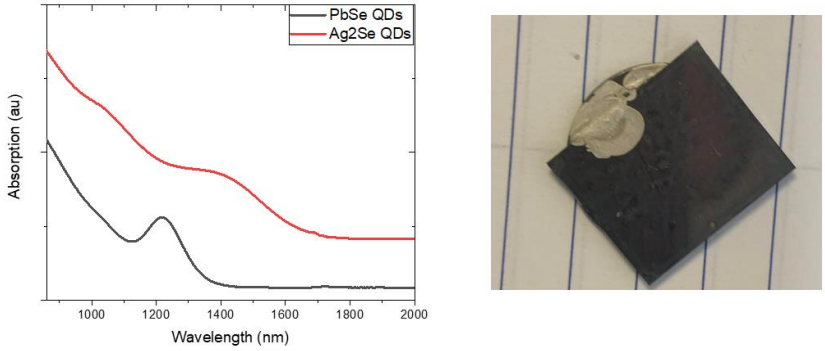

Figure 1: Absorption spectra of PbSe and Ag_2Se in-solution, note the spectra were offset for calrity (left). Photograph of one of the films used for KPFM measurement (right)

3. RESULTS AND DISCUSSION

3.1 Measurements on standard sample for calibration

Provided with the instrument is a standard sample containing aluminum, gold, and silicon which was used to calibrate the measurement. The work function values for each material on the standard sample is provided in *table* **1**[10] as you can see a range of values is reported rather than specific point values. The range of values is reported because factors such as oxygen absorption[11] and processing conditions[12],[13] have a direct impact on the work functions of materials and in some cases can even shift the work functions outside of this range. However, this range encompasses the values most commonly seen/used in literature so they can be used as good reference point for KPFM measurements.

Table 1: Work functions of different conductive materials on the standard sample provided.

Material	Work Function
Gold	5.1-5.47 eV
Silicon	4.6-4.85 eV
Aluminum	4.06-4.26 eV

KPFM measurements generally confirm the differences in work functions between the materials, see figure **2**, with gold clearly having the highest work function followed by silicon and then aluminum. Also shown in figure **2** is a single line scan to better show the difference in potential for the 3 materials. Using the potential value of the gold on this measurement as well as 9 others we assign the energy range of 5.1-5.47 eV to the potential of 354 mV ± 104 mV. The error reported here accounts for both the fluctuation seen during the same measurement as well as the variation in values across different measurements.

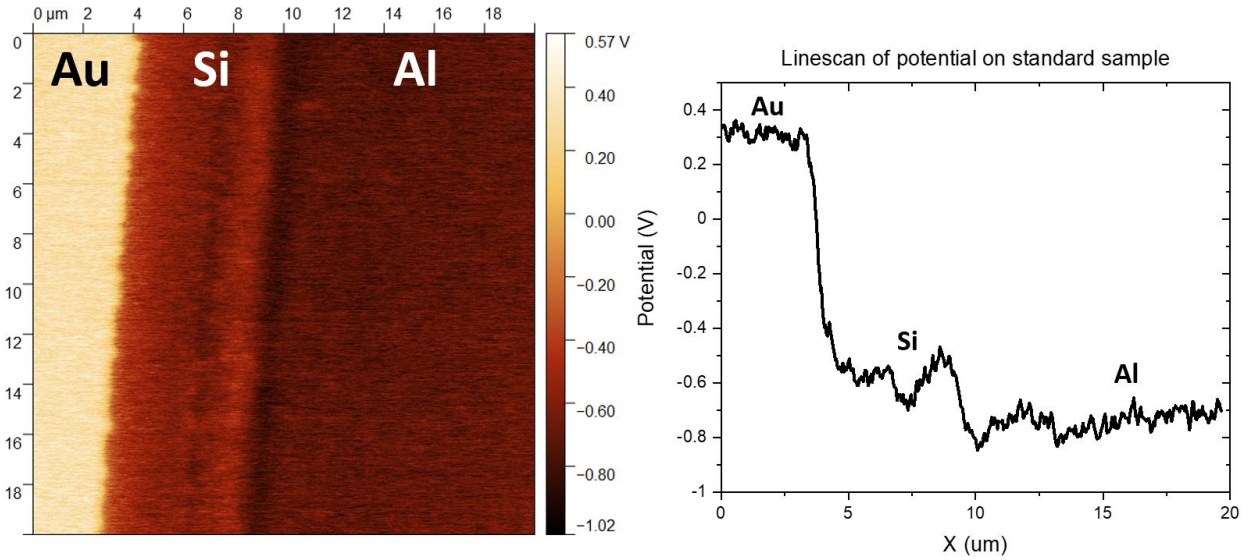

Figure 2*:* KPFM measurement of a standard sample with gold, silicon, and aluminum to compare difference in potential of each material (left). Line scan of the KPFM image on the left to better highlight the change as one moves from left to right across the sample (right).

3.2 Fermi level measurements on PbSe QD films

PbSe QD films showed potential values between 300-900 mV dependent on capping ligand, as can be seen in *figure* **3**, with OLA capped QD films having the lowest average potential value of 387 mV ± 104 mV. As expected, exchanging

OLA ligand for iodide-based ligands (NH_4I and KI) higher the Fermi level indicating an increase in the electron concentration in the film. Somewhat surprisingly the formic acid (FA) capped QD filmed showed the highest Fermi level, but the results are consistent with the high mobility values previously reported by Lin *et.al*[8]. Potential values were only moderately affected by the topography of the film (insets in *figure **3***), with some artifacts in the potential possibly being caused by the physical surface of the film (see *figure **3 b and c***). However, in most cases potential was relatively uniform throughout the entire measurement area as seen in *figure **3 a and d***. Artifacts, likely caused by impurities on the film surface (i.e. dirt), in the potential which could cause significant pumps or streaking were avoided because processing of surface potential is not recommended due to the possibility of changing values unwittingly.

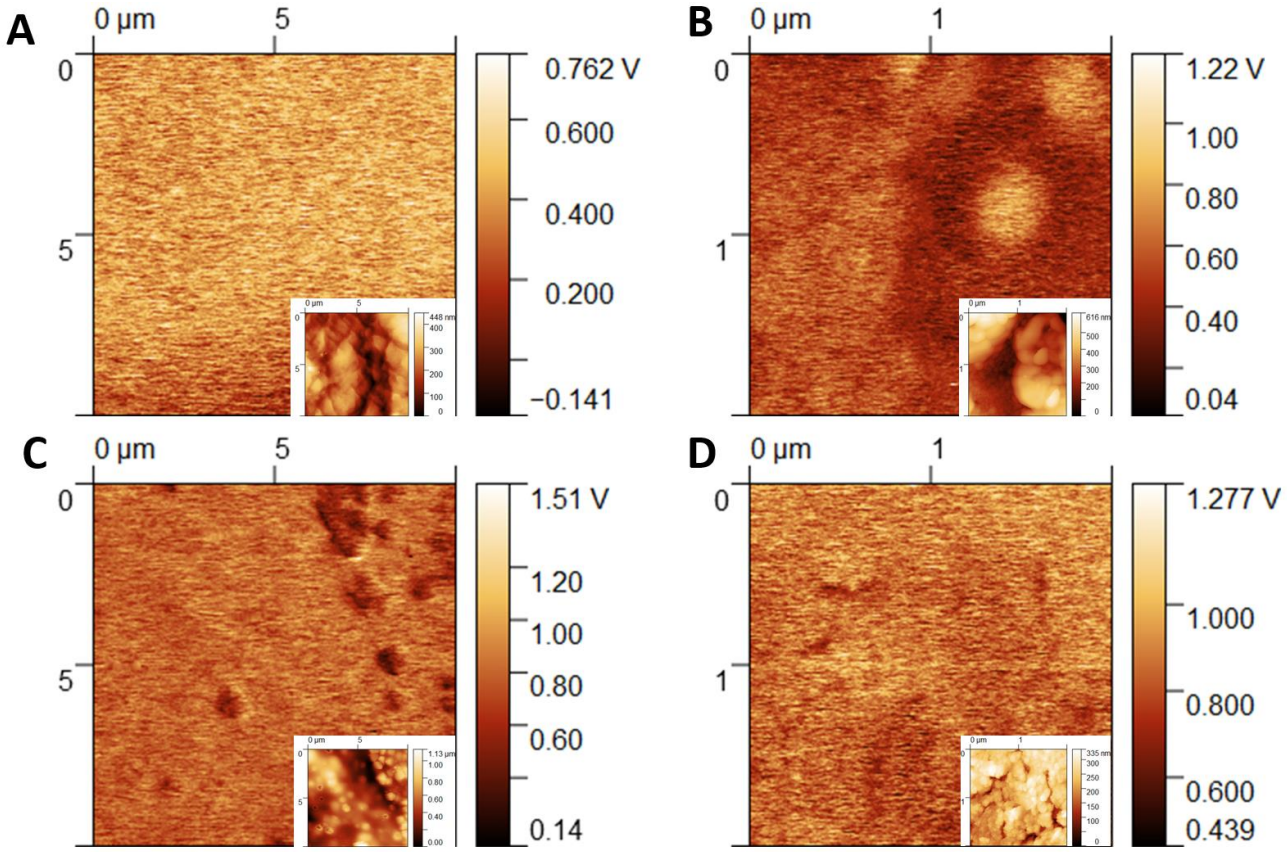

Figure 3*:* KPFM measurement of PbSe QD film with (A) oleylamine, (B) NH_4I, (C) KI, and (D) FA ligands respectively. Insets are the topography scans that accompany the potential scan.

A summary of all measurements of PbSe QD films is shown in *table **2***. The measured potentials of each film were converted into a Fermi level, by subtracting the average measured potential of gold (354 mV) from the average measured potential of the film and then adding this value to the tabulated work function value for gold. The reported errors account for both the error in the gold measurement and in the sample measurement.

Table 2: Measured surface potentials and calculated work functions of PbSe QD film with OLA, KI, NH_4I, and FA ligands.

PbSe QD film ligand	Measured potential value (mV)	Fermi level value relative to gold (eV)
Potassium Iodide (KI)	777 ± 108	5.52 - 5.89 eV ± 0.15 eV
Formic Acid (FA)	852 ± 90	5.6 - 5.97 eV ± 0.14 eV
Ammonium Iodide (NH_4I)	503 ± 108	5.25 – 5.62 eV ± 0.15 eV
Oleylamine (OLA)	387 ± 104	5.13 – 5.5 eV ± 0.15 eV

3.3 Fermi level measurements on Ag_2Se QD films

Ag_2Se QD films were measured in the same manner as PbSe QD films, and a variation of roughly 300 mV was seen from original OLA ligand to ZnI_2 ligand. All ligands show a higher potential value than the original oleylamine ligand, but the variation is not as strong as it was in the PbSe QD films, see *figure **4***. Given the large uncertainty in these measurements it is difficult to say that TBAI has measurably higher fermi level than OLA, even EDT could be questioned although that value is noticeably higher.

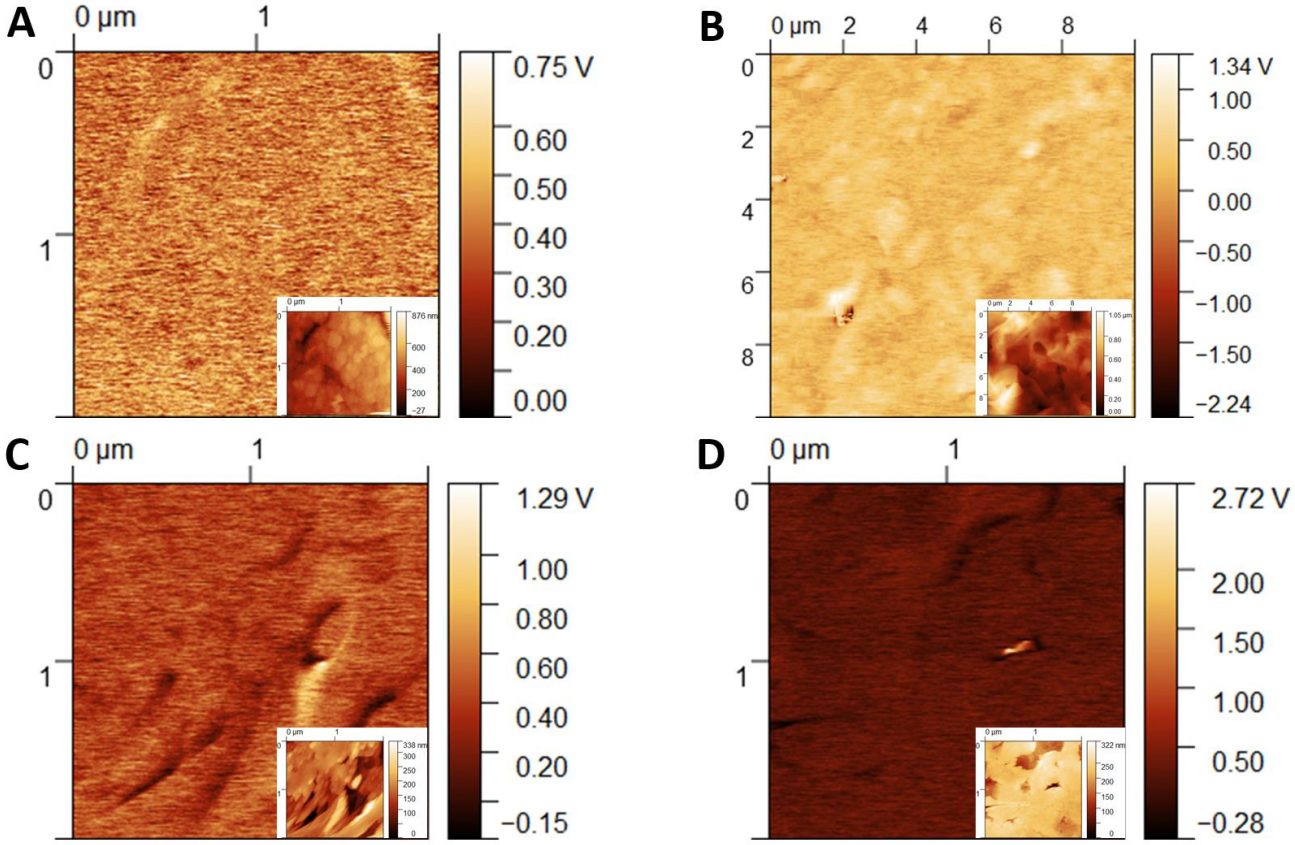

Figure 4*:* KPFM measurement of Ag_2Se QD film with (A) ZnI_2, (B) OLA, (C) EDT, and (D) TBAI ligands respectively. Insets are the topography scans that accompany the potential scan.

The results of all measurements on Ag_2Se QD films are summarized in *table **3***, the Fermi level was calculated in the same manner as it was for the PbSe QD films. The errors for the Ag_2Se QD films were generally larger, believed to be attributed to a solid-state ligand exchange procedure being used for ligand exchange rather than in-solution which was

utilized for PbSe QD films. The solid-state ligand exchange could increase the possibility of adding contaminants to the film surface as it is exposed to different solvents and the processing time is longer.

Table 3: Measured surface potentials and calculated work functions of Ag_2Se QD film with OLA, EDT, ZnI_2, and TBAI ligands.

Ag_2Se QD film ligand	Measured potential value (mV)	Fermi level value relative to gold (eV)
1,2- Ethanedithiol (EDT)	421 ± 120	5.17- 5.54 eV ± 0.16 eV
Tetrabutylammonium Iodide (TBAI)	291 ± 100	5.04 - 5.41 eV ± 0.14 eV
Oleylamine (OLA)	247 ± 163	5.00 - 5.37 eV ± 0.19 eV
Zinc Iodide (ZnI_2)	511 ± 172	5.26 - 5.63 eV ± 0.20 eV

4. CONCLUSIONS

KPFM is a powerful technique for determining the electrical properties of metals and semiconductors, sensitive enough to detect surface potential changes on the mV scale. We show a variance of nearly 300 mV in the Fermi level of Ag_2Se QD films based on choice of capping ligand, with an even greater variance of over 450 mV in PbSe QD films. Despite the usefulness of KPFM for determining Fermi levels relative to another material it still lacks the precision and repeatability required to be a tool that can be trusted to determine the absolute level relative to vacuum. The greatest obstacles to KPFM being used for absolute measurements are the variance in results from measurement to measurement, particularly when the AFM tip is exchanged. We typically saw very repeatable results when using the same tip (typically less than 50 mV variation from one measurement of the same sample to another), but that number changed drastically when another tip would be installed. For instance, the highest reading we saw for the gold sample standard was 540 mV while the lowest was 240 mV, resulting in 300 mV difference in potential for the same sample, the 540 mV reading was admittedly an outlier with the next highest average value being 450 mV. Another draw back of the technique is that the measurement is always relative to another control sample, and it is very difficult to find a material with a known work function that doesn't have a range of roughly 200 mV or even larger and isn't suspectable to change over time. For these reasons there will always be an inherent error associated with KPFM measurements when trying to determine an absolute energy level, but for direct comparison of 2 samples using the same tip KPFM is ideal.

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