A new approach to the modelling of Kelvin Probe Force Microscopy of heterostructures in dark and under illumination

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Abstract- **A numerical method is proposed to model Kelvin Probe Force Microscopy (KPFM) of heterostructures in the dark and under illumination. It is applied to FTO/TiO$_2$ and FTO/TiO$_2$/MAPbI$_3$ structures. Unexpected surface states on the top of the TiO$_2$ layers are revealed by combining the theoretical computation and experimental results. Basic features of KPFM under illumination are deduced as well, including surface photovoltage and surface photovoltage spectrum. It paves the way toward further investigations of more complicated optoelectronic devices.**

I. INTRODUCTION

The Kelvin probe force microscope (KPFM) was first developed in 1991 [1], to indirectly investigate interface or surface electronic properties, which are essential for nano-sized semiconductor devices. In KPFM, the surface potential of the sample is deduced relative to the fixed work-function of the uncontacted tip. In other words, KPFM allows a contactless electrical or even optical characterization of surfaces and/or interfaces in dark or under illumination [2]. In-situ or ex-situ applications of KPFM are useful for process monitoring and quality control of nano-sized devices, leading to cost and time saving. Moreover, it gives the opportunity to assess the quality of a layered structure before any irreversible degradation takes place.

II. NUMERICAL MODELING

A set of coupled equations including Poisson's equation, continuity and transport equations for electrons and holes densities are solved in Silvaco Atlas to model the KPFM. The photo-induced carrier generation processes are introduced through complex refractive index of the materials in addition to both bimolecular and trap-assisted recombination. The basic KPFM measurement setup is shown in figure 1. When the tip and the sample with different Fermi levels are electrically connected by a wire at their back and held close to each other on the other side, the electrons flow from one material to another along the wire till the Fermi levels are aligned. The unconnected surface is positive (negative) due to losing (adding) electrons, and electrostatic forces are obtained according to Coulomb's law. By applying an external bias between the two materials, the electrostatic force can be neutralized by the injecting electrons, when the external bias is equal to the initial difference between Fermi levels difference:

$$V_{CPD} = \frac{(E_{f.tip} - E_{f.sample})}{q}$$

where CPD is the abbreviation of Contact Potential Difference, and V$_{CPD}$ is the bias nullifying the electrostatic force. q is the elementary charge.
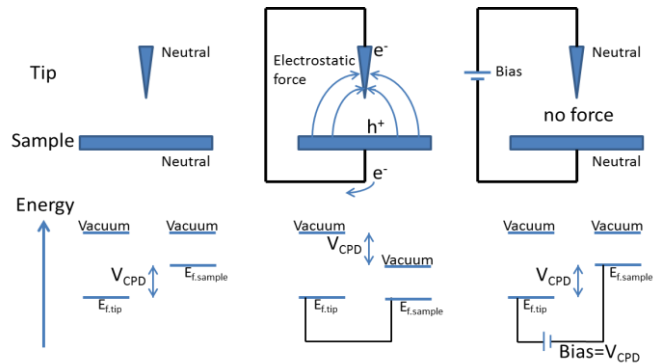

Fig. 1. Illustration of the basic setup of KPFM.

In the present work, halide perovskite solar cells (PSC), as a promising subject in photovoltaic field nowadays, is chosen for example to illustrate our model. Developing theoretical analyses of KPFM is attractive [3]. By comparison with published experimental works [4], [5], two architectures are modelled as shown in figure 2, F-SnO$_2$/TiO$_2$ and F-SnO$_2$/TiO$_2$/MAPbI$_3$. An insulator-like 10 nm thick air layer is inserted in the model to physically connect the tip and sample surfaces, and ensure the continuity of the potential. The material parameters of this fictitious air layer are the energy

band gap (E_g) of 12 eV, the electron affinity set to zero eV and the vacuum dielectric permittivity ε_0. The parameters for the other materials present in the heterostructures were defined in our previous work [6].
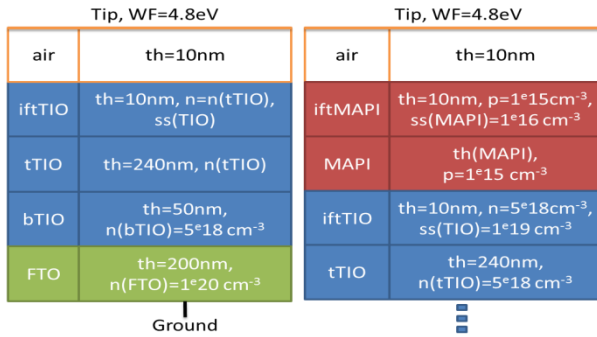

Fig. 2. Schematic of modelling architectures. bTIO, and tTIO are the bottom and top layer of TiO$_2$, respectively. MAPI is MAPbI$_3$ perovskite. And the ift indicates the top facial layer. ss is the surface state density.

III. SURFACE STATES AND WORK-FUNCTION

The termination of the periodic structure of a semiconductor at its free surface or interface may lead to the formation of a surface dipole and/or surface-localized electronic states, introducing carrier trap states within the semiconductor bandgap. Measured by KPFM [5], the surface work-function (WF) of highly n-doped TiO$_2$ can be as high as 4.5 eV on the top of FTO, or even 5.2 eV on the top of glass. We try to explain this phenomenon by taking surface states into account. The simulations with acceptor-like trap states on the TiO$_2$ surface have been done and are summarized in figure 3, while no change is observed in the case of donor-like ones. The surface trap states can increase the surface WF of TiO$_2$. An agreement between experiment and simulation is found when the doping level and surface state density of TiO$_2$ are 5^{E18} and 1^{E19} cm^{-3}, respectively.
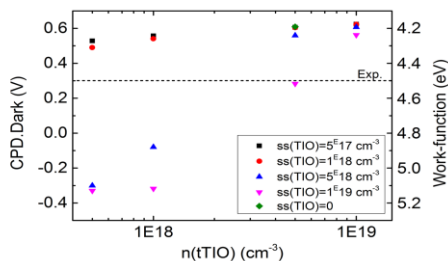

Fig. 3. Static contact potential difference (CPD.Dark) and work-function as a function of different doping levels, n(tTIO) and surface states, ss(TIO).

IV. SURFACE PHOTOVOLTAGE STUDIES IN KPFM

Since 1950s, the investigation of surface photovoltaic effects has focused on new methods and experimental tools for surface and bulk characterization. Relying on analyzing illumination-induced V_{CPD} changes in KPFM, the bandgap, the doping type, the carrier diffusion length and lifetime, and even energy levels in quantum structures and carrier accumulation in thin film structures can be assessed quantitatively now [2]. On the right of figure 2, a simple FTO/TIO$_2$/MAPbI$_3$ structure is designed to model surface photovoltage (SPV) and surface photovoltage spectrum (SPS). The back of the FTO is under one sun illumination. As shown on left of figure 4, the energy bandgap of MAPbI$_3$ around 1.55 eV is deduced from the SPV edge in agreement with the experimental absorption spectrum [7]. Furthermore, the SPV is calculated as a function of the thickness for the MAPbI$_3$ layer and presented on the right of figure 4. As predicted by the simulation, the KPFM technique is sensitive to the photo generated charges and the shallowly buried interface, and might be very helpful for process monitoring.
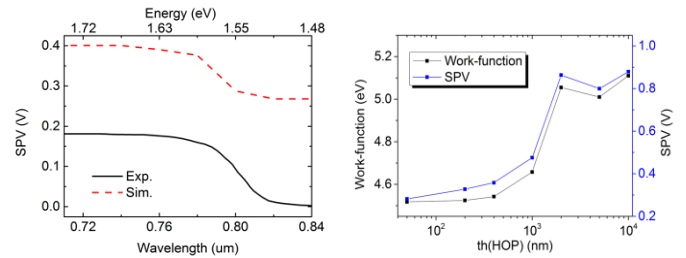

Fig. 4. Left) Simulated and experimental surface photovoltages spectroscopy (SPS). Right) Surface work-function and surface photovoltage (SPV) as a function of the thickness for the intrinsic MAPbI$_3$ layers (th(HOP)).

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